

Efficient ortho-para conversion of H_2 on interstellar grain surfaces

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Abstract

Context. Fast surface conversion between ortho- and para- H_2 has been observed in laboratory studies, and this mechanism has been proposed to play a role in the control of the ortho-para ratio in the interstellar medium. Observations of rotational lines of H_2 in Photo-Dissociation Regions (PDRs) have indeed found significantly lower ortho-para ratios than expected at equilibrium. The mechanisms controlling the balance of the ortho-para ratio in the interstellar medium thus remain incompletely understood, while this ratio can affect the thermodynamical properties of the gas (equation of state, cooling function).

Aims. We aim to build an accurate model of ortho-para conversion on dust surfaces based on the most recent experimental and theoretical results, and to validate it by comparison to observations of H_2 rotational lines in PDRs.

Methods. We propose a statistical model of ortho-para conversion on dust grains with fluctuating dust temperatures, based on a master equation approach. This computation is then coupled to full PDR models and compared to PDR observations.

Results. We show that the observations of rotational H_2 lines indicate a high conversion efficiency on dust grains, and that this high efficiency can be accounted for if taking dust temperature fluctuations into account with our statistical model of surface conversion. Simpler models neglecting the dust temperature fluctuations do not reach the high efficiency deduced from the observations. Moreover, this high efficiency induced by dust temperature fluctuations is quite insensitive to the values of microphysical parameters of the model.

Conclusions. Ortho-para conversion on grains is thus an efficient mechanism in most astrophysical conditions that can play a significant role in controlling the ortho-para ratio.

Key words. astrochemistry - ISM: molecules - molecular processes - ISM: dust, extinction - ISM: photon-dominated region (PDR) - methods: numerical

1. Introduction

H_2 is the main constituent of molecular clouds. It can be observed in absorption in diffuse gas, and in emission in warm gas and/or high UV field conditions (mainly photodissociation regions, hereafter PDRs, and shocks). Its low rotational levels are collisionally excited and trace the gas temperature in the emitting material, while its vibrational levels are either pumped by the UV radiation field or collisionally excited in hot shocked material. Excitation at formation has also been proposed to contribute to vibrational excitation.

H_2 in the diffuse ISM has thus mainly been observed in absorption (Savage et al. 1977; Rachford et al. 2002; Tumlinson et al. 2002; Gry et al. 2002; Richter et al. 2003; Lacour et al. 2005; Gillmon et al. 2006; Rachford et al. 2009), with the only observation in emission being Falgarone et al. (2005). The excitation temperature of the first two rotational levels (T_{01}) is commonly used as a measure of the gas temperature in diffuse clouds, although it could stop being a meaningful measure at low $N(\text{H}_2)$ (Srianand et al. 2005; Roy et al. 2006). Higher rotational levels appear suprathermally excited and could trace a small fraction of warm gas heated by the dissipation of interstellar turbulence in shocks or vortices (Gredel et al. 2002; Godard et al. 2014; Bron 2014).

Observed in emission in brighter PDRs (Fuente et al. 1999; Moutou et al. 1999; Habart et al. 2003, 2004; Allers et al. 2005; Thi et al. 2009; Fleming et al. 2010; Habart et al. 2011; Sheffer et al. 2011), it traces the surface layer of warm molecular gas close to the H/H_2 transition, and can be used as a diagnostics of the gas temperature and UV radiation field. It can also help in constraining processes such as H_2 formation or photoelectric heating (Habart et al. 2004, 2011).

H_2 has also been observed in extragalactic environments. Observations of rotational emission in other galaxies has shown that the overall H_2 emission could be explained by PDRs (Naslim et al. 2015 in the LMC, Roussel et al. 2007 in the SINGS galaxy sample, Higdon et al. 2006 in ULIRGs) except in Seyfert galaxies where a significant shock contribution might be present (Rigopoulou et al. 2002; Pereira-Santaella et al. 2014). In addition, H_2 has been detected in absorption in DLAs (Ledoux et al. 2003; Noterdaeme et al. 2007; Muzahid et al. 2015).

H_2 exists as two spin isomers : para- H_2 with the spins of its two nucleus in opposite directions, and ortho- H_2 with parallel nuclear spins. In the ground electronic state, ortho- H_2 can only have an odd rotational number J , while para- H_2 only takes even rotational numbers. As conversion between the two spin isomers is forbidden for an isolated molecule (e.g., Pachucki & Komasa 2008: radiative transition rate of $6 \times 10^{-14} \text{ yr}^{-1}$) and only reactive collisions can induce conversion, the ortho-to-para ratio (hereafter OPR) can be out of local thermal equilibrium (hereafter LTE). At LTE, the OPR is close to 3 at high temperatures

(> 200 K) and goes to zero at low temperatures. The ratio between the successive rotational lines of H₂ can thus be affected by an out-of-equilibrium OPR, and the interpretation of H₂ emission requires a good understanding of the OPR. Moreover, the excitation temperature T_{01} used in absorption studies only traces the gas temperature if the OPR is thermalized.

Several observations have derived out-of-equilibrium OPR values from the pure rotational lines of H₂ in PDRs (Fuente et al. 1999; Moutou et al. 1999; Habart et al. 2003; Fleming et al. 2010; Habart et al. 2011), with OPR values ~ 1 , significantly lower than the value of ~ 3 expected from the excitation temperature of the low- J rotational lines. Out-of-equilibrium rotational OPR values have also been reported in the SINGS galaxy sample by Roussel et al. (2007). Note that this is a different problem than the low values of the OPR derived from vibrational lines of H₂. Low OPR values in the vibrational levels can be caused by preferential UV pumping of para-H₂ due to preferential self-shielding of ortho-H₂ even when the true OPR (dominated by the $v = 0$ levels) is 3, as described in great detail in Sternberg & Neufeld (1999).

In dark dense clouds, H₂ cannot be directly observed, and the OPR can only be determined indirectly. For instance, Troscompt et al. (2009) deduce the OPR from the anomalous absorption of H₂CO owing to the different collisional rates with ortho-H₂ and para-H₂. Maret & Bergin (2007) use DCO⁺, as the fractionation reaction $\text{H}_3^+ + \text{HD} \rightleftharpoons \text{H}_2\text{D}^+ + \text{H}_2$ is very sensitive to the OPR of H₂. Pagani et al. (2009) similarly use the influence of the OPR on the deuterium chemistry and deduce the OPR from observations of N₂D⁺, N₂H⁺ and H₂D⁺. All find an OPR higher than the LTE value in cold gas. Non dissociative shocks, in which the quickly heated gas makes H₂ observable in emission but does not have time to significantly change its OPR, can also offer a way to estimate the OPR in the preshock dark molecular gas (Neufeld et al. 2006; Yuan & Neufeld 2011).

The OPR of H₂ plays several important roles in the physico-chemistry of the interstellar medium. First, it can affect significantly the dynamics of core formation through gravitational collapse in star forming clouds by modifying the heat capacity and the equation of state of the gas, as was shown by Vaytet et al. (2014) who compared numerical simulations with different prescriptions corresponding to LTE OPR or fixed OPR of 3. Second, it controls large parts of the chemistry in dense clouds, such as the nitrogen chemistry (Dislaire et al. 2012; Faure et al. 2013) through the reaction $\text{N}^+ + \text{H}_2 \rightleftharpoons \text{NH}^+ + \text{H}$, or the deuterium chemistry (Flower et al. 2006) through the fractionation reaction $\text{H}_3^+ + \text{HD} \rightleftharpoons \text{H}_2\text{D}^+ + \text{H}_2$. Finally, the slow conversion process between the two spin isomers has been used as a tool to measure the age of molecular clouds (Pagani et al. 2011, 2013).

The OPR is controlled by several processes, as first investigated by Burton et al. (1992) :

- Formation is usually assumed to occur with an OPR of 3 but this value is uncertain (Takahashi 2001; Yabushita et al. 2008; Gavilan et al. 2012).
- Photo-dissociation can sometimes destroy para-H₂ preferentially due to the faster self-shielding of ortho-H₂ when the OPR is > 1 . This can lead to the OPR being locally > 3 (Abgrall et al. 1992; Sternberg & Neufeld 1999).
- Reactive collisions can induce conversion between the two spin isomers. The main conversion reactions are proton exchange with H⁺ (Gerlich 1990; Honvault et al. 2011) and with H₃⁺ (Gómez-Carrasco et al. 2012), and hydrogen exchange with H (Schulz & Le Roy 1965; Truhlar 1976; Mandy & Martin 1992, 1993; Sun & Dalgarno 1994; Lique

et al. 2012). This last reaction possesses an activation barrier (~ 5000 K) and is thus only efficient in warm gas. Reactive collisions with H₂ have an even higher activation barrier (~ 60000 K, Carmona-Novillo et al. 2007) and are usually neglected. These reactions tend to thermalize the OPR to the gas temperature.

- H₂ molecules that are adsorbed on the surface of dust grains can interact with the magnetic fields caused by impurities and surface defects and convert from one spin isomer to the other (Fukutani & Sugimoto 2013, and references therein). This process is the subject of the present article and tends to thermalize the OPR to the dust temperature, which is significantly lower than the gas temperature in PDRs.

An approximate treatment of ortho-para conversion on dust was used in Le Bourlot (2000) to investigate the effect of this process in PDRs. The process was found to be only efficient on cold dust grains. It was then shown that with a few hypotheses favoring high efficiency (high binding energy, low dust temperatures), the pure rotational lines of H₂ were strongly affected. Sheffer et al. (2011) found that PDR models could successfully explain observed OPR values lower than LTE in the PDR NGC 2023 South when including this process with the high efficiency hypothesis of Le Bourlot (2000).

In this article, we investigate the efficiency of this process using a detailed model based on the most recent experimental and theoretical results reviewed by Fukutani & Sugimoto (2013). As the surface processes are highly sensitive to the dust temperature and as small dust grains are known to have fluctuating temperatures that can significantly affect the efficiency of surface processes (e.g., Bron et al. 2014 for H₂ formation), we build a statistical model of ortho-para conversion on dust grains with temperature fluctuations, which we compare to a simpler rate equation model without fluctuations. We then investigate the effect of this process in PDR models and compare the predicted observable OPR values to PDR observations.

In Sect. 2, we present the physical processes at play and define their rates. We also present a simple rate equation model neglecting the temperature fluctuations for comparison with the more sophisticated model that we develop in the following sections. In Sect. 3, we present the statistical method that we employ to compute the effect of dust temperature fluctuations on ortho-para conversion on grains. Sect. 4 presents the results of this statistical computation and discusses the importance of the various microphysical parameters. In Sect. 5, we couple this statistical computation of the ortho-para conversion rate to the Meudon PDR Code to study the impact of this new computation on full PDR models, and confront their results to observations of the ortho-para ratio in PDRs. Finally we give our conclusions in Sect. 6.

2. Processes and rate equation model

We will consider dust grains of sizes above 1 nm. Ortho-para conversion on Polycyclic Aromatic Hydrocarbons (PAHs) is probably much less efficient due to the lack of surface defects and impurity sites which are thought to allow ortho-para conversion on graphite surfaces.

We adopt a simple spherical grain model. We note a the grain radius, and assume uniformly distributed adsorption sites on the surface, characterized equivalently by the surface density of sites n_s , the typical distance between sites d_s or the total number of

sites N_s . Those quantities are related by

$$N_s = 4\pi a^2 n_s = \frac{4\pi a^2}{d_s^2}.$$

In addition, we note T_d the grain temperature, T_{gas} the gas temperature, n_o and n_p respectively the number of ortho-H₂ and para-H₂ molecules physisorbed on the grain surface, and $n(\text{H}_2^{(o)})$ and $n(\text{H}_2^{(p)})$ respectively the gas phase densities of ortho- and para-H₂.

We now describe the different processes affecting the adsorbed H₂ molecules that we include in our model.

2.1. Adsorption of molecular hydrogen

The first step of ortho-para conversion of an H₂ molecule is physisorption on the grain surface, in which the molecule binds to the grain through van der Waals interactions. A gas H₂ molecule hitting the grain on an empty site becomes physisorbed with a probability $S(T_{\text{gas}})$ called the sticking probability. We discuss the choice of this sticking function below. We assume rejection if the molecule hits an occupied site. The rates of adsorption of ortho-H₂ and para-H₂ molecules on the grain (in s⁻¹) are thus

$$k_{\text{coll}}^{(i)} S(T_{\text{gas}}) \left(1 - \frac{n_o + n_p}{N_s} \right) \quad (1)$$

with $k_{\text{coll}}^{(i)} = \pi a^2 n(\text{H}_2^{(i)}) \sqrt{\frac{8k_B T_{\text{gas}}}{\pi 2m_H}}$, with $i = o$ for ortho-H₂ and $i = p$ for para-H₂. In the following, we will note $k_{\text{ads}}^{(i)} = k_{\text{coll}}^{(i)} S(T_{\text{gas}})$ to simplify the notations.

Few measurements of the sticking function for H₂ on dust surfaces have been made. The only full measurement as a function of the gas temperature is given by Matar et al. (2010), who measured the sticking function on amorphous water ice in the temperature range 30 – 350 K. They give the prescription :

$$S(T_{\text{gas}}) = S_0 \frac{1 + \beta \frac{T_{\text{gas}}}{T_0}}{\left(1 + \frac{T_{\text{gas}}}{T_0} \right)^\beta} \quad (2)$$

with $S_0 = 0.76$, $T_0 = 87$ K and $\beta = 5/2$. This formula is derived from a statistical model of sticking on amorphous surfaces, fitted to the experimental results.

This sticking function is shown on Fig. 1 (blue curve). Theoretical calculation have also been presented in Leitch-Devlin & Williams (1985) and are also shown on the graph: 0.4 for graphite and 0.05 for silicates at ~ 100 K. In the present paper, our comparison to observations will focus on rotational H₂ emission in PDRs. In the regions of interest, ice mantles are thus not yet present, and we need sticking functions on bare carbonaceous and silicate surfaces. As we lack precise determinations of these sticking functions, and as the Matar et al. (2010) sticking function is compatible with the value for graphite from Leitch-Devlin & Williams (1985), we will use this sticking function (Eq. 2) for all models in this article. The surface ortho-para conversion efficiency is directly proportional to the sticking coefficient, so that a lower sticking coefficient would proportionally reduce the importance of surface conversion.

In comparison Acharyya (2014) determined lower limits to the sticking coefficient of H₂ on olivine as a function of temperature for a very limited range of gas temperatures (7-14 K).

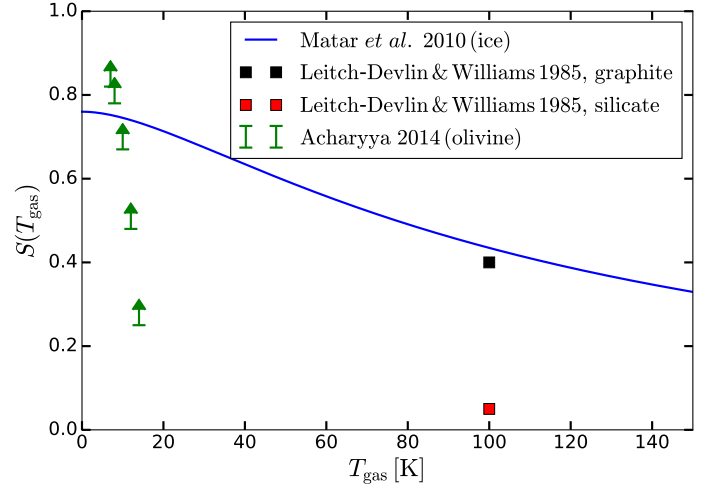


Figure 1. Sticking coefficients of H₂ on different grain surfaces from the literature.

These lower limits are also presented on Fig. 1 and seem to indicate a steeper decrease with temperature, but the limited range of temperatures and the fact that they are only lower limits make conclusions difficult to draw.

2.2. Ortho-para conversion

Once physisorbed, an ortho-H₂ molecule can convert to a para-H₂ molecule with rate $k_{o \rightarrow p}(T_d)$, and vice versa with rate $k_{p \rightarrow o}(T_d)$. Conversion occurs because of electro-magnetic interactions with the surface allowing spin-transfer through various processes, and often involves impurity sites or surface defects (see Fukutani & Sugimoto 2013 and Ilisca & Ghiglieno 2014 for recent overviews of these processes).

Those two rates are related by the fact that for an adsorbed population of H₂ without desorption or arrival, the populations of ortho-H₂ and para-H₂ at equilibrium must yield an equilibrium ortho-para ratio. We thus have

$$\frac{k_{p \rightarrow o}(T_d)}{k_{o \rightarrow p}(T_d)} = \text{OPR}^{(\text{eq})}(T_d) \quad (3)$$

We will neglect here the fact that the energy levels of physisorbed H₂ are slightly modified compared to the gas phase values, and take the gas phase equilibrium OPR function.

Several experiments, which we discuss below, have measured a conversion timescale τ_{conv} to pure para-H₂ on a cold surface. In such experiments, H₂ is first adsorbed on the surface with some initial OPR. As the temperature of the surface is very low, it then progressively converts to para-H₂. Desorption is negligible. In such case, the evolution matrix is

$$\begin{pmatrix} -k_{p \rightarrow o}(T_d) & k_{o \rightarrow p}(T_d) \\ k_{p \rightarrow o}(T_d) & -k_{o \rightarrow p}(T_d) \end{pmatrix} \quad (4)$$

with eigenvalues $k_{p \rightarrow o}(T_d) + k_{o \rightarrow p}(T_d)$ and 0. The measured characteristic time is thus

$$\tau_{\text{conv}} = \frac{1}{k_{p \rightarrow o}(T_d) + k_{o \rightarrow p}(T_d)} \quad (5)$$

We note that this characteristic time scale is related to the half-life that is often used by $t_{\text{half-life}} \simeq 0.69 \tau_{\text{conv}}$.

From Eq. 3 and 5, we can deduce expressions for the conversion rate coefficients :

$$\begin{cases} k_{o \rightarrow p}(T_d) = \frac{1}{\tau_{\text{conv}}} \frac{1}{1 + \text{OPR}^{(\text{eq})}(T_d)} \\ k_{p \rightarrow o}(T_d) = \frac{1}{\tau_{\text{conv}}} \frac{\text{OPR}^{(\text{eq})}(T_d)}{1 + \text{OPR}^{(\text{eq})}(T_d)} \end{cases} \quad (6)$$

Because we lack experimental determinations of the temperature dependance of τ_{conv} , we will take it as a constant.

Several experiments have measured the ortho-para conversion timescale:

A few experiments have measured the conversion timescale on graphite. The first measurement was done by Kubik et al. (1985), who measured a conversion rate of 0.40%/h (characteristic time $\tau_{\text{conv}} \sim 10^4$ s) for H₂ ortho-para conversion, and of 0.069%/h ($\tau_{\text{conv}}^{(\text{D}_2)} \sim 5 \times 10^6$ s) for D₂ para-ortho conversion. Another measurement was performed by Palmer & Willis (1987) at a surface temperature of 10 K, finding full conversion for H₂ in less than 1 min ($\tau_{\text{conv}} < 20$ s). Finally, Yucel et al. (1990) measured the para-ortho conversion of D₂ and found a conversion time of 20 min at 10 K. Assuming the same ratio between the H₂ ortho-para conversion rate and the D₂ para-ortho conversion rate as found in Kubik et al. (1985), this would lead to a conversion timescale of 2.5 s for H₂, in agreement with Palmer & Willis (1987). Yucel et al. (1990) also showed that the conversion timescale increases with the surface coverage, and that it is roughly constant with temperature in the range 10-25 K, and increases sharply to ~ 70 min at 8 – 10 K.

On amorphous water ice, several measurements have been made. The oldest estimation is Sandler (1954), giving a conversion half-life of ~ 10 h ($\tau_{\text{conv}} \sim 5 \times 10^4$ s) on solid D₂O at 90 K. Hixson et al. (1992) then measured a half-time of ~ 40 min ($\tau_{\text{conv}} \sim 3.6 \times 10^3$ s) on solid D₂O at 12 K. They proposed the presence of different kinds of sites, some of which having enhanced conversion. They also suspect a low level of oxygen contamination. Amiaud et al. (2008) found no detectable para-ortho conversion of D₂ at 10 K on a time of $\sim 10^3$ s ($\tau_{\text{conv}}^{(\text{D}_2)} > 2 \times 10^4$ s). Watanabe et al. (2010) experimental results seem to indicate a conversion of the order of 10 – 20% in 20 min at 15 K ($\tau_{\text{H}_2} = 5 \times 10^3 - 1 \times 10^4$ s). Chehrouri et al. (2011) find that the conversion is helped by co-adsorbed O₂. In the presence of O₂ they find a conversion time of ~ 220 s, while in the absence of O₂, they find a rate less than 15%/h ($\tau_{\text{H}_2} > 2 \times 10^4$ s). In contrast, Sugimoto & Fukutani (2011) measure a conversion timescale in the range 230 – 710 s on clean ice at 10 K, and propose a theoretical model predicting a timescale of the order of $\sim 10^2$ s.

These values are gathered in Table 1. The results are thus quite contradictory, and we will have to explore values of the conversion timescale in the range 1 – 10^4 s. The most likely value seems to be 1 – 10 s on graphite, and $10^2 - 10^4$ s on ices.

2.3. Thermal desorption

In competition with the conversion process, the H₂ molecule can also desorb thermally from the surface. The thermal desorption rate of ortho- and para-H₂ is determined by their physisorption energies. Several studies have measured the adsorption energy of H₂ on various surfaces, most of which do not distinguish between ortho- and para-H₂. As para-H₂ is insensitive to the anisotropic part of the adsorption potential while ortho-H₂ is not, ortho-H₂ tends to have a higher binding energy than para-H₂ (Fukutani & Sugimoto 2013).

For crystalline silicates, Katz et al. (1999) give an adsorption energy of 27.1 meV (314.5 K). For amorphous silicates, Vidali et al. 2007; Perets et al. 2007 find that the distribution of binding energies can be described with two values : 35 meV (406 K) and 53 meV (615 K). Vidali & Li 2010 determine the full distribution of binding energies and find a distribution with a peak at 57 meV (662 K), and extending from 45 meV (522 K) to 90 meV (1044 K). For amorphous carbon, Katz et al. (1999) give 46.7 meV (542 K). For amorphous water ice (ASW), Manicò et al. (2001) find 63 meV (731 K). Roser et al. (2002) study the binding energy distribution for various types of ices, describing the distribution by two energy values. They find 45 meV (522 K) and 68 meV (789 K) for heat-treated low density ASW, 39 meV (453 K) and 67 meV (778 K) for vapor-deposited low density ASW, and 53 meV (615 K) and 69 meV (801 K) for high density ice. Finally, Buch et al. (1993) give the only measurement of the binding energy difference between ortho- and para-H₂ on an astrophysically relevant surface: amorphous water ice. Experimentally, they find a lower limit on the adsorbed OPR of 9 at 12 K before conversion has time to take place, corresponding to a difference between ortho- and para-binding energies $\Delta T_{\text{phys}} \geq 13$ K. They also study numerically the distribution of binding energies for both ortho and para-H₂ on amorphous water ice, and find for para-H₂ a binding energy of 646 ± 177 K, and a difference between the ortho- and para- binding energies of 30 ± 16 K.

These values of the binding energy are summarized in Table 2. Overall, a value of 500 – 600 K seems reasonable for both amorphous carbons and amorphous silicates, a value of 315 K for crystalline silicates, and a value in the range 500 – 800 K for amorphous water ices. We will thus explore a range of binding energies between 300 and 800 K. In addition, we will investigate the effect of an ortho/para difference in binding energies by testing both without difference and with a difference of 30 K.

The desorption rates of ortho- and para-H₂ (for one molecule) are then

$$k_{\text{des}}^{(i)}(T_d) = v_0^{(i)} \exp \left(- \frac{T_{\text{phys}}^{(i)}}{T_d} \right) \quad (7)$$

with $i = o$ for ortho-H₂ and $i = p$ for para-H₂, and where the v_0 's are typical vibration frequencies given by (Hasegawa et al. 1992)

$$v_0^{(i)} = \frac{1}{\pi} \sqrt{\frac{2 k_B T_{\text{phys}}^{(i)}}{d_0^2 m_{\text{H}}}} \quad (8)$$

with $d_0 = 0.1$ nm the typical width of the potential well.

2.4. Photon emission and absorption

These surface processes are sensitive to the grain temperature. This temperature is controlled by the absorption and emission of photons by the grain, which we model as in Bron et al. (2014).

The power received by the grain at a photon energy U is $P_{\text{abs}}(U) = 4\pi^2 a^2 Q_{\text{abs}}(U) I_U(U)$, with $Q_{\text{abs}}(U)$ the absorption efficiency coefficient of the grain at photon energy U , and $I_U(U)$ the radiation field intensity at photon energy U (in units of $\text{W} \cdot \text{m}^{-2} \cdot \text{J}^{-1} \cdot \text{sr}^{-1}$). Later, we need transition rates between thermal energy states of the grain. The rate of photon absorptions at this energy U is

$$R_{\text{abs}}(U) = \frac{P_{\text{abs}}(U)}{U}. \quad (9)$$

Table 1. Experimental measurements of the ortho-para conversion timescale on different surfaces. See the text for details.

Reference	Surface	Temperature (K)	$\tau_{\text{conv}}^{\text{H}_2}$ (s)	$\tau_{\text{conv}}^{\text{D}_2}$ (s)
(1)	Graphite	< 12	10^4	5×10^6
(2)	Graphite	10	< 20	-
(3)	Graphite	10	-	1.2×10^3
(4)	Water Ice	90	5×10^4	-
(5)	Water Ice	12	3.6×10^3	-
(6)	Water Ice	10	-	$> 2 \times 10^4$
(7)	Water Ice	15	$5 \times 10^3 - 1 \times 10^4$	-
(8)	Water Ice (co-adsorbed O ₂)	10	2.2×10^2	-
	Water Ice (clean)		$> 2 \times 10^4$	-
(9)	Water Ice (clean)	10	$2.3 \times 10^2 - 7.1 \times 10^2$	-

(1) : Kubik et al. (1985); (2) : Palmer & Willis (1987); (3) : Yucel et al. (1990); (4) : Sandler (1954); (5) : Hixson et al. (1992); (6) : Amiaud et al. (2008); (7) : Watanabe et al. (2010); (8) : Chehrouri et al. (2011); (9) : Sugimoto & Fukutani (2011)

Table 2. Experimental and theoretical determinations of the binding energy of H₂ on different surfaces. See the text for details.

Reference	Surface	T_{phys} (K)	Note
(1)	Crystalline silicate	314.5	-
(2)	Amorphous silicates	406 and 615	Binding energy distribution described by two values
(3)	Amorphous silicates	662 ([522 – 1044])	Binding energy distribution
(1)	Amorphous carbon	542	-
(4)	Amorphous water ice	646 ± 177	Binding energy difference between ortho-H ₂ and para-H ₂ $\Delta T_{\text{phys}} = 30 \pm 16$ K
(5)	Amorphous water ice	731	-
(6)	Amorphous water ice (heat-treated low density)	522 and 789	-
	Amorphous water ice (vapor-deposited low density)	453 and 778	Binding energy distribution described by two values
	Amorphous water ice (high density)	615 and 801	-

(1) : Katz et al. (1999); (2) : Perets et al. 2007; (3) : Vidali & Li 2010; (4) : Buch et al. (1993); (5) : Manicò et al. (2001); (6) : Roser et al. (2002)

We approximate the grain emission by a modified black body law with a specific intensity $Q_{\text{abs}}(U) B_U(U, T_d)$, where $B_U(U, T)$ is the usual black body specific intensity. The power emitted at photon energy U is then $P_{\text{em}}(U, T_d) = 4\pi^2 a^2 Q_{\text{abs}}(U) B_U(U, T_d)$ and the photon emission rate is

$$R_{\text{em}}(U, T_d) = \frac{P_{\text{em}}(U, T_d)}{U}. \quad (10)$$

These events occur randomly as Poisson processes and cause fluctuations of the grain temperature. The impact of these fluctuations on the efficiency of ortho-para conversion on dust grains is investigated in details in the following sections. In the simpler rate equation treatment that we will use for comparison, we neglect these fluctuations and use the usual equilibrium temperature T_{eq} of the grain, defined by the balance between the instantaneous emitted and absorbed powers :

$$\int_0^{+\infty} dU P_{\text{abs}}(U) = \int_0^{E_{\text{eq}}} dU P_{\text{em}}(U, T_{\text{eq}}), \quad (11)$$

where the upper bound on the right hand side accounts for the finite total energy of the grain (E_{eq} is the thermal energy of the grain at the equilibrium temperature, related to T_{eq} by $E_{\text{eq}} = \int_0^{T_{\text{eq}}} C(T) dT$, with $C(T)$ the heat capacity of the grain).

In the following, we use a standard interstellar radiation field (Mathis et al. 1983) and apply a scaling factor χ to the

UV component of the field. We measure the UV intensity of those fields using the usual $G_0 = \frac{1}{u_{\text{Habing}}} \int_{912\text{\AA}}^{2400\text{\AA}} d\lambda u_{\lambda}(\lambda)$, where $u_{\text{Habing}} = 5.3 \times 10^{-15} \text{ J m}^{-3}$. G_0 is related to χ as $G_0 \simeq 0.65 \chi$.

The dust properties ($C(T_d)$, $Q_{\text{abs}}(U)$ and ρ) are taken from Compiegne et al. (2011) and the DustEM code¹. We consider amorphous carbon and silicate dust populations and use the properties used in this reference (see references therein, in their Appendix A).

2.5. Rate equation model at constant temperature

We will compare the results of our statistical treatment presented in the next section to a simpler rate equation model that neglects dust temperature fluctuations, and that we present in this section. In this simple model, the grain is thus supposed to be at a constant temperature T_d , for which we take the equilibrium temperature defined by Eq. 11.

Using the rates of the different processes defined above, we can thus write a system of rate equations :

¹ Available at <http://www.ias.u-psud.fr/DUSTEM/>.

$$\begin{cases} \frac{dn_o}{dt} = k_{\text{ads}}^{(o)} \left(1 - \frac{n_o + n_p}{N_s} \right) - n_o k_{\text{des}}^{(o)}(T_d) \\ \quad - n_o k_{o \rightarrow p}(T_d) + n_p k_{p \rightarrow o}(T_d) \\ \frac{dn_p}{dt} = k_{\text{ads}}^{(p)} \left(1 - \frac{n_o + n_p}{N_s} \right) - n_p k_{\text{des}}^{(p)}(T_d) \\ \quad - n_p k_{p \rightarrow o}(T_d) + n_o k_{o \rightarrow p}(T_d) \end{cases} \quad (12)$$

At equilibrium, we find

$$n_o = \frac{k_{\text{ads}}^{(o)} \left(\frac{k_{\text{ads}}^{(p)}}{N_s} + k_{\text{des}}^{(p)}(T_d) + k_{p \rightarrow o}(T_d) \right) + k_{\text{ads}}^{(p)} \left(k_{p \rightarrow o}(T_d) - \frac{k_{\text{ads}}^{(o)}}{N_s} \right)}{D(T_d)} \quad (13)$$

and

$$n_p = \frac{k_{\text{ads}}^{(p)} \left(\frac{k_{\text{ads}}^{(o)}}{N_s} + k_{\text{des}}^{(o)}(T_d) + k_{o \rightarrow p}(T_d) \right) + k_{\text{ads}}^{(o)} \left(k_{o \rightarrow p}(T_d) - \frac{k_{\text{ads}}^{(p)}}{N_s} \right)}{D(T_d)} \quad (14)$$

with

$$D(T_d) = \left(\frac{k_{\text{ads}}^{(o)}}{N_s} + k_{\text{des}}^{(o)}(T_d) + k_{o \rightarrow p}(T_d) \right) \left(\frac{k_{\text{ads}}^{(p)}}{N_s} + k_{\text{des}}^{(p)}(T_d) + k_{p \rightarrow o}(T_d) \right) - \left(k_{o \rightarrow p}(T_d) - \frac{k_{\text{ads}}^{(p)}}{N_s} \right) \left(k_{p \rightarrow o}(T_d) - \frac{k_{\text{ads}}^{(o)}}{N_s} \right) \quad (15)$$

To evaluate the efficiency of the ortho-para conversion process, we first define the net ortho-para conversion rate (in s⁻¹) on the grain surface as

$$k_{O/P}^{(\text{grain})} = n_o k_{o \rightarrow p} - n_p k_{p \rightarrow o}. \quad (16)$$

The net conversion rate is positive when conversion occurs in the usual ortho-to-para direction, and negative if para-to-ortho conversion occurs. This latter case could happen if the grains are warmer than the gas.

We then define the ortho-para conversion efficiency as

$$\eta_{O/P}^{(\text{grain})} = \frac{k_{O/P}^{(\text{grain})}}{k_{\text{coll}}^{(o)} S(T_{\text{gas}})} \quad (17)$$

which represents the fraction of the ortho-H₂ molecules sticking to the grain that are converted to para-H₂ (in a stationary situation). Note that we took the parts that depend on the gas conditions (density, temperature) out of our definition of the conversion efficiency, in order to separate the effects of the sticking coefficient from the surface conversion process. Note also that this definition is only meaningful if conversion occurs in the ortho-to-para direction, which will be the case in our applications.

In this constant temperature rate equation model, the results are not directly affected by the grain size, except through the equilibrium temperature which is size dependent. We will thus show here a few results as a function of dust temperature.

As the conversion efficiency is controlled by the competition between conversion and desorption (an ortho-H₂ molecule needs to have time to convert before desorbing), the two main parameters affecting this efficiency are the binding energy T_{phys} , which controls the desorption rate, and the conversion timescale τ_{conv} .

Fig. 2 shows the impact of the binding energy on the conversion efficiency. In all cases, the efficiency curves are bell-shaped, with a flat top at full efficiency. At high temperature,

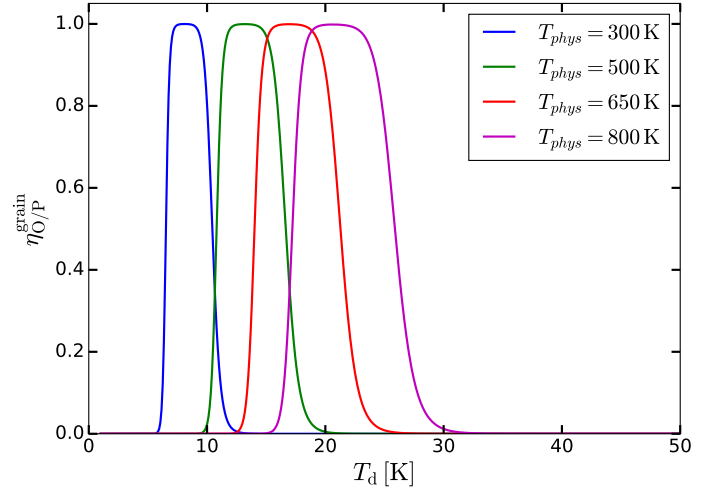


Figure 2. Conversion efficiency as a function of the grain temperature for different para-H₂ binding energies in the constant temperature rate equation model. The gas ortho-para ratio is taken as 3, and the conversion timescale at 10s.

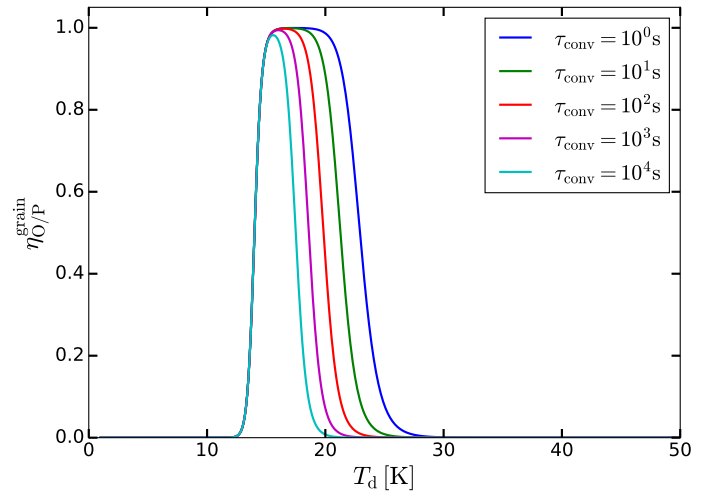


Figure 3. Conversion efficiency as a function of the grain temperature for different conversion timescale in the constant temperature rate equation model. The gas ortho-para ratio is taken as 3, and the binding energy at 650 K.

desorption is too fast and the adsorbed H₂ molecules do not have time to convert from ortho to para. At low temperature, H₂ molecules cover all the surface as desorption is very slow, and most molecules coming from the gas are rejected. The range of temperature where conversion is efficient is thus very limited.

The width and position of the efficiency window is strongly affected by the binding energy, going from 7 – 10 K for $T_{\text{phys}} = 300$ K to 17 – 26 K for $T_{\text{phys}} = 800$ K. Consequently, this model predicts that in PDR conditions where the grains are exposed to a strong UV field and are thus warmer than this efficiency window (typically 30 – 50 K for small grains), ortho-para conversion on dust grain should be inefficient. We will see in the following sections that taking into account the dust temperature fluctuations significantly changes this picture.

Fig. 3 shows the influence of the conversion timescale. It only affects the upper limit of the efficiency window as the lower limit is due to rejection and controlled by the competition between adsorption and desorption. Its impact is less than that of the binding energy as the conversion rate is inversely propor-

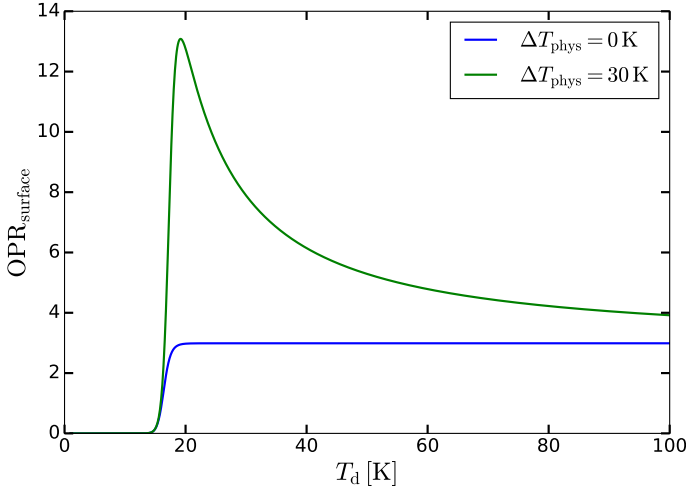


Figure 4. Ortho-para ratio of the adsorbed molecules, with and without a difference of binding energy ΔT_{phys} between ortho-H₂ and para-H₂. This computation was done with a gas ortho-para ratio of 3, a binding energy for para-H₂ of 500 K and a conversion timescale of 10s.

tional to this timescale, while the desorption rate depends exponentially on the binding energy. It can still double the width of the efficiency window over the range of relevant values.

Finally, Fig. 4 shows how a difference in binding energy ΔT_{phys} between ortho-H₂ and para-H₂ affects the OPR of the adsorbed molecules. At low temperature, conversion is much faster than desorption and the OPR on the surface is very low. When desorption starts to become significant, para-H₂ desorbs faster than ortho-H₂ and the surface population is enriched in ortho-H₂ leading to a surface OPR significantly higher than 3. This enrichment could play a role for further surface reactions leading to more complex molecules. A higher binding energy for ortho-H₂ than for para-H₂ also makes the high efficiency window slightly larger, but the effect is small compared to the effects of the other parameters described above.

3. Method for a stochastic model

We will now take into account the dust temperature fluctuations. We are interested in the average conversion efficiency under the effect of these fluctuations in a statistically stationary situation. It is thus sufficient to compute the stationary probability density function (hereafter PDF) of the state of the grain, $f(T_d, n_o, n_p)$, from which all average quantities of interest can be deduced. In the following, we will note T the instantaneous temperature of the grain to simplify the notations. Moreover, we will work with the thermal energy of the grain E rather than its temperature T . The two are related by

$$E(T) = \int_0^T dT' C(T') \quad (18)$$

where $C(T)$ is the heat capacity of the grain. Conversely, we will also note $T(E)$ the temperature corresponding to thermal energy E .

3.1. General master equation

As the state of the system evolves in time by discrete events (photon absorption or emission, adsorption, desorption or conversion of a molecule), the evolution of its PDF is governed by

a master equation of the form

$$\frac{df(X)}{dt} = \int_{\text{states}} dY f(Y) p_{Y \rightarrow X} - \int_{\text{states}} dY f(X) p_{X \rightarrow Y} \quad (19)$$

where X generically describes the state of the system, and $p_{X \rightarrow Y}$ are the transition rates from state X to state Y . The integrals are to be interpreted as integrals over the continuous state variables (e.g., the thermal energy E of the grain) and sums over the discrete state variables (e.g., the number n_o of ortho-H₂ molecules on the surface).

The transition rates of the possible events are

$$\begin{cases} E, n_o, n_p \rightarrow E' > E, n_o, n_p : & R_{\text{abs}}(E' - E) \\ E, n_o, n_p \rightarrow E' < E, n_o, n_p : & R_{\text{em}}(E - E', T(E)) \\ E, n_o, n_p \rightarrow E, n_o + 1, n_p : & k_{\text{ads}}^{(o)} \left(1 - \frac{n_o + n_p}{N_s}\right) \\ E, n_o, n_p \rightarrow E, n_o, n_p + 1 : & k_{\text{ads}}^{(p)} \left(1 - \frac{n_o + n_p}{N_s}\right) \\ E, n_o, n_p \rightarrow E, n_o - 1, n_p : & n_o k_{\text{des}}^{(o)}(T_{\text{grain}}) \\ E, n_o, n_p \rightarrow E, n_o, n_p - 1 : & n_p k_{\text{des}}^{(p)}(T_{\text{grain}}) \\ E, n_o, n_p \rightarrow E, n_o - 1, n_p + 1 : & n_o k_{o \rightarrow p}(T_{\text{grain}}) \\ E, n_o, n_p \rightarrow E, n_o + 1, n_p - 1 : & n_p k_{p \rightarrow o}(T_{\text{grain}}) \\ \text{all other cases} : & 0 \end{cases} \quad (20)$$

Writing explicitly the terms corresponding to the different processes in Eq. 19 and considering statistical equilibrium, we get the stationary master equation governing $f(E, n_o, n_p)$:

$$\begin{aligned} & \int_0^E dE' R_{\text{abs}}(E - E') f(E', n_o, n_p) \\ & + \int_E^{+\infty} dE' R_{\text{em}}(E' - E, T(E')) f(E', n_o, n_p) \\ & + k_{\text{ads}}^{(o)} \left(1 - \frac{n_o + n_p - 1}{N_s}\right) f(E, n_o - 1, n_p) \\ & + k_{\text{ads}}^{(p)} \left(1 - \frac{n_o + n_p - 1}{N_s}\right) f(E, n_o, n_p - 1) \\ & + (n_o + 1) k_{\text{des}}^{(o)}(T(E)) f(E, n_o + 1, n_p) \\ & + (n_p + 1) k_{\text{des}}^{(p)}(T(E)) f(E, n_o, n_p + 1) \\ & + (n_o + 1) k_{o \rightarrow p}(T(E)) f(E, n_o + 1, n_p - 1) \\ & + (n_p + 1) k_{p \rightarrow o}(T(E)) f(E, n_o - 1, n_p + 1) = \\ & f(E, n_o, n_p) M(E, n_o, n_p) \end{aligned} \quad (21)$$

where

$$\begin{aligned} M(E, n_o, n_p) = & \int_0^E dE' R_{\text{em}}(E - E', T(E)) + \int_E^{+\infty} dE' R_{\text{abs}}(E' - E) \\ & + k_{\text{ads}}^{(o)} \left(1 - \frac{n_o + n_p}{N_s}\right) + k_{\text{ads}}^{(p)} \left(1 - \frac{n_o + n_p}{N_s}\right) + n_o k_{\text{des}}^{(o)}(T(E)) \\ & + n_p k_{\text{des}}^{(p)}(T(E)) + n_o k_{o \rightarrow p}(T(E)) + n_p k_{p \rightarrow o}(T(E)) \end{aligned} \quad (22)$$

As boundary conditions, $f(E, n_o, n_p) = 0$ if $n_o < 0$, $n_p < 0$, $E < 0$ or $n_o + n_p > N_s$.

Directly solving this equation numerically would be extremely time-consuming as the unknown is a function of three variables. We can however simplify the problem by noting that all the average quantities of interest can be expressed in terms of the marginal thermal energy PDF

$$f_E(E) = \sum_{n_o, n_p} f(E, n_o, n_p) \quad (23)$$

and of the conditional expectation for the ortho and para populations at a given instantaneous thermal energy

$$\langle n_o | E \rangle = \sum_{n_o, n_p} n_o \frac{f(E, n_o, n_p)}{f_E(E)} \quad (24)$$

and

$$\langle n_p | E \rangle = \sum_{n_o, n_p} n_p \frac{f(E, n_o, n_p)}{f_E(E)} \quad (25)$$

For instance, the average conversion efficiency (using the definition by Eq. 17)

$$\begin{aligned} \langle \eta_{O/P}^{(\text{grain})} \rangle = & \int_0^{+\infty} dE \sum_{n_o, n_p} \frac{n_o k_{o \rightarrow p}(T(E)) - n_p k_{p \rightarrow o}(T(E))}{k_{\text{coll}}^{(o)} S(T_{\text{gas}})} f(E, n_o, n_p) \end{aligned} \quad (26)$$

can also be expressed as

$$\begin{aligned} \langle \eta_{O/P}^{(\text{grain})} \rangle = & \int_0^{+\infty} dE \frac{\langle n_o | E \rangle k_{o \rightarrow p}(T(E)) - \langle n_p | E \rangle k_{p \rightarrow o}(T(E))}{k_{\text{coll}}^{(o)} S(T_{\text{gas}})} f_E(E) \end{aligned} \quad (27)$$

We will thus compute three single-variable functions rather than one 3-variable function. We now deduce the equations governing these three functions.

3.2. Marginal temperature equation

We start by deriving the equation governing the marginal thermal energy PDF. This equation can be deduced from the main master equation Eq. 19.

By applying $\sum_{n_o=0, n_p=0}^{n_o+n_p \leq N_s}$ to Eq. 19, we get

$$\begin{aligned} P(E) f_E(E) = & \int_0^E dE' R_{\text{abs}}(E - E') f_E(E') \\ & + \int_E^{+\infty} dE' R_{\text{em}}(E' - E, T(E')) f_E(E') \end{aligned} \quad (28)$$

with

$$P(E) = \int_E^{+\infty} dE' R_{\text{abs}}(E' - E) + \int_0^E dE' R_{\text{em}}(E - E', T(E)) \quad (29)$$

This equation governs the marginal PDF $f_E(E)$ of the thermal energy of the grain, which describes the stationary statistics of the temperature fluctuations. It was already encountered in Bron et al. (2014) when studying the impact of dust temperature fluctuations on H₂ formation on grain surfaces. We use here the same numerical resolution method, consisting in iteratively applying the operator

$$\mathcal{L}[f](E) = \frac{\int_0^E dE' R_{\text{abs}}(E - E') f_E(E') + \int_E^{+\infty} dE' R_{\text{em}}(E' - E, T(E')) f_E(E')}{P(E)} \quad \text{and}$$

to an initial guess until some convergence criterium is met.

The thermal energy PDF f_E can be converted into the temperature PDF f_T using the usual variable change rule for PDFs:

$$f_T(T) = f_E(E) C(T) \quad (31)$$

3.3. Marginal population equations

We now deduce the equations governing the conditional expectation of the ortho and para populations. Applying the operators $\sum_{n_o=0, n_p=0}^{n_o+n_p \leq N_s} n_o \times \cdot$ and $\sum_{n_o=0, n_p=0}^{n_o+n_p \leq N_s} n_p \times \cdot$ to Eq. 19 yields the system of equations governing $\langle n_o | E \rangle$ and $\langle n_p | E \rangle$:

$$\begin{aligned} & \int_0^E dE' R_{\text{abs}}(E - E') \frac{f_E(E')}{f_E(E)} \langle n_o | E' \rangle \\ & + \int_E^{+\infty} dE' R_{\text{em}}(E' - E, T(E')) \frac{f_E(E')}{f_E(E)} \langle n_o | E' \rangle = \\ & - k_{\text{ads}}^{(o)} + T_{\text{op}}(E) \langle n_p | E \rangle + T_{\text{oo}}(E) \langle n_o | E \rangle \end{aligned} \quad (32)$$

and

$$\begin{aligned} & \int_0^E dE' R_{\text{abs}}(E - E') \frac{f_E(E')}{f_E(E)} \langle n_p | E' \rangle \\ & + \int_E^{+\infty} dE' R_{\text{em}}(E' - E, T(E')) \frac{f_E(E')}{f_E(E)} \langle n_p | E' \rangle = \\ & - k_{\text{ads}}^{(p)} + T_{\text{po}}(E) \langle n_o | E \rangle + T_{\text{pp}}(E) \langle n_p | E \rangle \end{aligned} \quad (33)$$

where

$$T_{\text{op}}(E) = \frac{k_{\text{ads}}^{(o)}}{N_s} - k_{p \rightarrow o}(T(E)) \quad (34)$$

$$T_{\text{oo}}(E) = P(E) + k_{o \rightarrow p}(T(E)) + \frac{k_{\text{ads}}^{(o)}}{N_s} + k_{\text{des}}^{(o)}(T(E)) \quad (35)$$

$$T_{\text{po}}(E) = \frac{k_{\text{ads}}^{(p)}}{N_s} - k_{o \rightarrow p}(T(E)) \quad (36)$$

$$T_{\text{pp}}(E) = P(E) + k_{p \rightarrow o}(T(E)) + \frac{k_{\text{ads}}^{(p)}}{N_s} + k_{\text{des}}^{(p)}(T(E)) \quad (37)$$

This is a system of coupled inhomogeneous second-kind Fredholm equations. Similarly to the situation encountered in Bron et al. (2014) with a similar equation, the discretized version of this system gives a linear system that converges exponentially fast towards a singular system when the grain size a grows. To avoid numerical problems, we use the same trick as in Bron et al. (2014) and eliminate the constant terms $-k_{\text{ads}}^{(o)}$ and $-k_{\text{ads}}^{(p)}$ to get a system of homogeneous second-kind Fredholm equation that can be solved by the same iterative method as the marginal temperature equation in the previous section.

By multiplying equations 32 and 33 by $f_E(E)$ and integrating over E , we obtain

$$\begin{aligned} k_{\text{ads}}^{(o)} = & \int_0^{+\infty} dE' T_{\text{op}}(E') f_E(E') \langle n_p | E' \rangle \\ & + \int_0^{+\infty} dE' T'_{\text{oo}}(E') f_E(E') \langle n_o | E' \rangle \end{aligned} \quad (38)$$

$$\begin{aligned} (30) \quad k_{\text{ads}}^{(p)} = & \int_0^{+\infty} dE' T_{\text{po}}(E') f_E(E') \langle n_o | E' \rangle \\ & + \int_0^{+\infty} dE' T'_{\text{pp}}(E') f_E(E') \langle n_p | E' \rangle \end{aligned} \quad (39)$$

with $T'_{\text{oo}}(E) = T_{\text{oo}}(E) - P(E)$ and $T'_{\text{pp}}(E) = T_{\text{pp}}(E) - P(E)$.

Injecting equations 38 and 39 into equations 32 and 33, we get

$$\begin{aligned} \int_0^{+\infty} dE' \left[\frac{G(E, E')}{f(E)} + T'_{oo}(E') \right] f_E(E') \langle n_o | E' \rangle \\ + \int_0^{+\infty} dE' T'_{op}(E') f_E(E') \langle n_p | E' \rangle = \\ T_{op}(E) \langle n_p | E \rangle + T_{oo}(E) \langle n_o | E \rangle \end{aligned} \quad (40)$$

and

$$\begin{aligned} \int_0^{+\infty} dE' \left[\frac{G(E, E')}{f_E(E)} + T'_{pp}(E') \right] f_E(E') \langle n_p | E' \rangle \\ + \int_0^{+\infty} dE' T'_{po}(E') f_E(E') \langle n_o | E' \rangle = \\ T_{po}(E) \langle n_o | E \rangle + T_{pp}(E) \langle n_p | E \rangle \end{aligned} \quad (41)$$

with

$$G(E, E') = \begin{cases} R_{abs}(E - E') & \text{if } E' < E \\ R_{em}(E' - E, T(E')) & \text{if } E' > E \end{cases} \quad (42)$$

Equations 40 and 41 are now homogeneous.

Finally, we can rewrite this system in vector form as

$$\begin{pmatrix} T_{oo}(E) & T_{op}(E) \\ T_{po}(E) & T_{pp}(E) \end{pmatrix}^{-1} \times \int_0^{+\infty} dE' \begin{pmatrix} \left[\frac{G(E, E')}{f(E)} + T'_{oo}(E') \right] f_E(E') & T_{op}(E') f_E(E') \\ T_{po}(E') f_E(E') & \left[\frac{G(E, E')}{f_E(E)} + T'_{pp}(E') \right] f_E(E') \end{pmatrix} \begin{pmatrix} \langle n_o | E' \rangle \\ \langle n_p | E' \rangle \end{pmatrix} = \begin{pmatrix} \langle n_o | E \rangle \\ \langle n_p | E \rangle \end{pmatrix} \quad (43)$$

where the integral sign is to be applied to each component of the vector. The first matrix is always invertible, as can be easily verified by expressing its determinant.

This equation shows that the solution is an eigenvector associated with eigenvalue 1 for the linear integral operator defined by the left-hand side. After discretization of the problem, we numerically compute such an eigenvector, and we then normalize it using equations 38 and 39. Once $f_E(E)$, $\langle n_o | E \rangle$ and $\langle n_p | E \rangle$ are computed, we can compute all the average quantities of interest.

4. Results

We now present the results of this computation of the ortho-para conversion efficiency taking into account the dust temperature fluctuations. We first discuss how the temperature fluctuations change significantly the efficiency in PDR-like conditions, before investigating the influence of the microphysical parameters of the model. When not specified otherwise, our standard model consists of amorphous carbon grains with a binding energy of H₂ $T_{phys} = 550$ K and a conversion timescale $\tau_{conv} = 10$ s.

4.1. Efficiency of the conversion process in PDR-like conditions

We will present the results in terms of the average conversion efficiency defined by Eq. 27. Fig. 5 shows this average conversion efficiency for a single grain as a function of grain size, and for different ambient UV radiation field intensities G_0 . The results of the full statistical computation (solid lines) are compared to

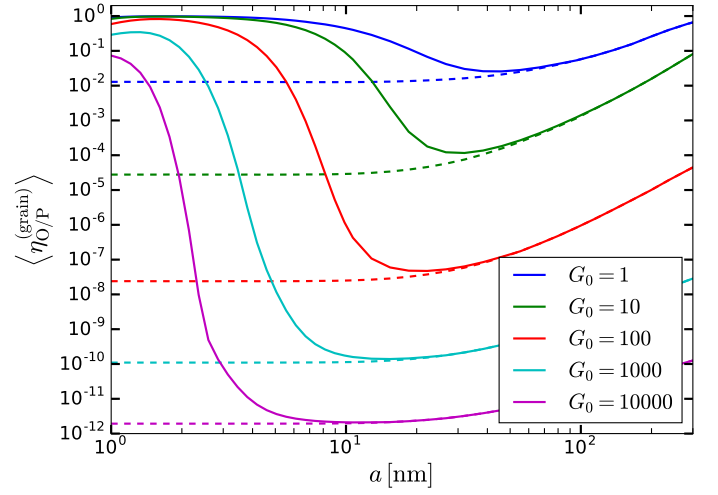


Figure 5. Conversion efficiency on one grain as a function of grain size for different radiation field intensities G_0 . Solid lines : Full statistical model, dashed lines : rate equation model without dust temperature fluctuations.

those of the simpler rate equation model which neglects the dust temperature fluctuations (dashed lines).

In the rate equation model, the grains are assumed to be at constant temperature at their equilibrium temperature. As discussed in Sect. 2.5, the ortho-para conversion process is then only efficient when the grains are sufficiently cold. The rate equation model thus only approaches full efficiency for the largest grains, and gives efficiencies that decrease sharply with the radiation field intensities for all sizes. Under $G_0 = 1$, the efficiency is of the order of a few percents for most sizes.

The full statistical model gives significantly different results. For large grains, UV photons (limited to the Lyman limit in PDRs) do not have enough energy to cause significant fluctuations of the dust temperature. The full model and the rate equation model thus give the same efficiencies for large grains. For small grains, the full model finds efficiencies orders of magnitude higher than the rate equation model. There seems to be a critical size below which conversion occurs at almost full efficiency. This critical size distinguishes small grains for which the temperature PDF is wide enough to overlap with the high efficiency window found in Sect. 2.5 from large grains whose narrow temperature PDF falls entirely outside this window. Small grains thus spend a very large fraction of their time at low temperatures, where conversion is efficient, between very short high temperature spikes during which desorption becomes dominant.

These temperature PDFs can be seen in Fig. 6 in the case of an external radiation field with $G_0 = 100$ (corresponding to the red curve on Fig. 5). Grains of size 1 nm and 3 nm have very wide temperature PDFs with a large probability around 10 – 20 K, corresponding to the cold state of grains between high-temperature spikes caused by UV-photon absorption (the high-temperature spikes correspond here to the long low-probability high-temperature tails for these sizes). This temperature range also corresponds to the high conversion efficiency window found in Sect. 2.5, which explains why we find high conversion efficiency for these grain sizes in Fig. 5. In comparison, the temperature PDFs for sizes of 10, 30 and 100 nm are not wide enough to cover the high efficiency window and these grain sizes have much lower conversion efficiencies.

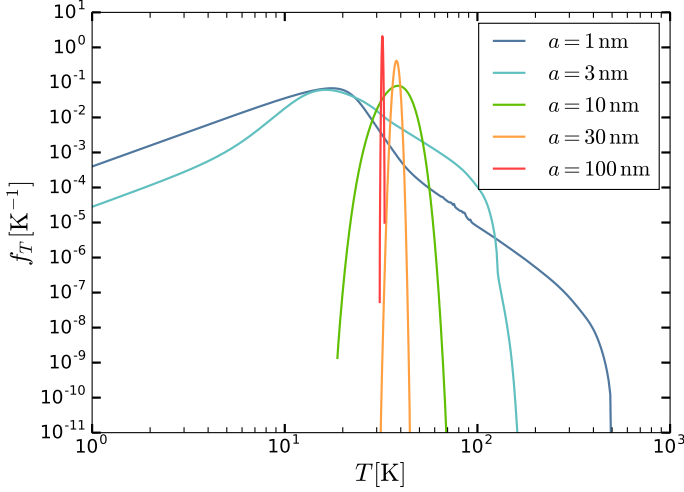


Figure 6. Temperature PDF of amorphous carbon grains of various sizes under an external UV field with $G_0 = 100$.

In order to evaluate the resulting overall efficiency, we can then integrate the average net conversion rate

$$\langle k_{\text{O/P}}^{(\text{grain})} \rangle = \int dE (\langle n_{\text{o}} | E \rangle k_{\text{o} \rightarrow \text{p}}(T(E)) - \langle n_{\text{p}} | E \rangle k_{\text{p} \rightarrow \text{o}}(T(E))) f_E(E) \quad (44)$$

over the full dust size distribution to obtain the overall net conversion rate

$$k_{\text{O/P}}^{(\text{tot.})} = \int da f_a(a) \langle k_{\text{O/P}}^{(\text{grain})}(a) \rangle \quad (45)$$

where $f_a(a)$ is the dust size distribution. We then define the overall conversion efficiency as

$$\eta_{\text{O/P}}^{\text{tot.}} = \frac{k_{\text{O/P}}^{(\text{tot.})}}{k_{\text{coll}}^{(\text{o})} \text{tot.} S(T_{\text{gas}})} \quad (46)$$

where

$$k_{\text{coll}}^{(\text{o})} \text{tot.} = \int da f_a(a) k_{\text{coll}}^{(\text{o})}(a) \quad (47)$$

is the total collision rate of ortho-H₂ on grains.

In this section, we use a simplified dust population comprising only amorphous carbon grains from 1 nm to 0.3 μm with a MRN-like (Mathis et al. 1977) power-law size distribution with exponent -3.5 . As we assume that conversion is inefficient on PAHs, not including them in our dust population does not affect the results.

Fig. 7 shows the resulting total conversion efficiency for the full dust distribution as a function of UV intensity G_0 . The results of the full statistical computation (solid line) are again compared to those of the rate equation model without fluctuations (dashed lines). In the rate equation model, we saw on Fig. 5 that all sizes excepted the largest had low efficiencies that were sharply decreasing when increasing the UV intensity. As small grains represent most of the dust surface in our dust population, the overall conversion efficiency in the rate equation model is never higher than a few percents and decreases quickly when G_0 is increased. In the full model, the smallest grains had their efficiencies almost unaffected by the UV intensity. As they dominate the total dust surface available for conversion, the overall

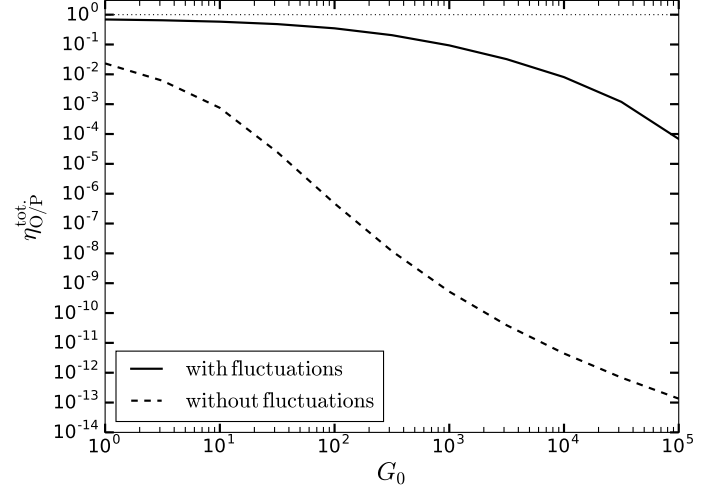


Figure 7. Global conversion efficiency for a full dust size distribution as a function of the UV intensity G_0 .

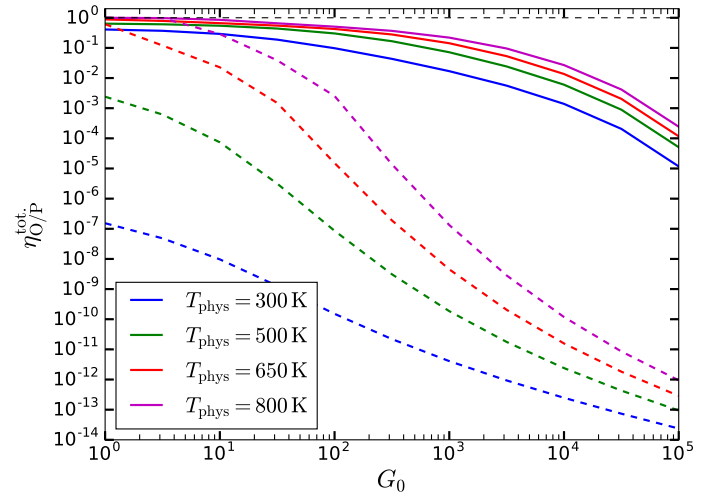


Figure 8. Global conversion efficiency as a function G_0 for different values of the binding energy of H₂, T_{phys} .

conversion efficiency is much less affected by G_0 and remains above 10% up to $G_0 = 1000$.

Dust temperature fluctuations thus make ortho-para conversion on grains efficient in most PDR conditions, because small grains, which dominate the total surface and undergo large temperature fluctuations, spend a large fraction of their time at low temperature between the temperature spikes caused by photon absorption events. Note that this efficiency does not include the sticking efficiency.

4.2. Influence of the microphysical parameters

We now investigate the impact of the uncertainties in the microphysical parameters. The two most important parameters are the binding energy T_{phys} , which controls the desorption rate, and the conversion timescale τ_{conv} , which controls the conversion rate.

Fig. 8 shows the effect of the binding energy T_{phys} on both the rate equation model (dashed lines) and the full statistical model. While the rate equation model is strongly sensitive to the value of the binding energy (seven order of magnitude difference at low G_0 between $T_{\text{phys}} = 300$ K and 800 K), the effect on the full statistical model is much smaller. As T_{phys} is decreased, the high

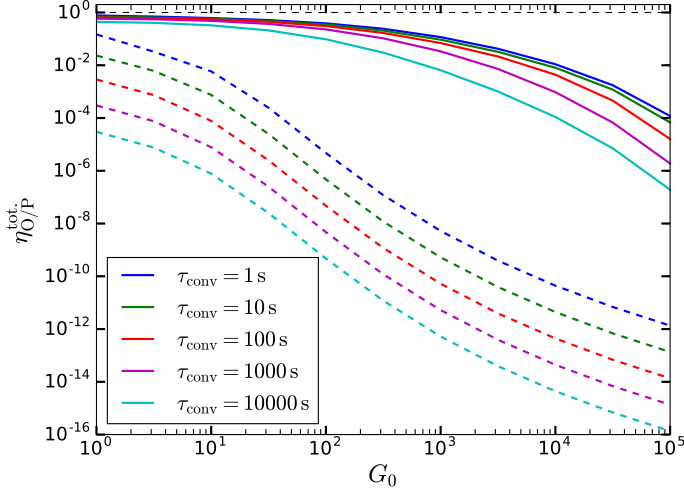


Figure 9. Global conversion efficiency as a function G_0 for different values of the conversion timescale τ_{conv} .

efficiency window described in Sect. 2.5 is shifted to lower temperature. In the rate equation model where a grain has a single constant temperature, this temperature will at some point fall out of the efficiency window, resulting in a sharply decreasing efficiency. In contrast, small grains in the full statistical model have a wide temperature PDF. As the efficiency window is shifted, it will still be covered by the tails of the PDF, resulting in a much smoother decrease of the efficiency. The uncertainties on the binding energies thus only cause uncertainties on the efficiency of at most slightly more than one order of magnitude, instead of the seven orders of magnitude uncertainty when neglecting the fluctuations.

Fig. 9 shows similarly the impact of the uncertainties on τ_{conv} . A similar effect is observed, although less dramatic. While in the rate equation models, the uncertainties on τ_{conv} cause a four orders of magnitude difference in the efficiency, the full model is almost unaffected up to $G_0 \simeq 100$, and gives differences of slightly more than two orders of magnitude at most for the strongest UV fields.

The dust temperature fluctuations thus significantly reduce the impact of the uncertainties about the microphysical parameters. Uncertainties of typically one or two orders of magnitude still remain on the final conversion efficiency.

5. PDR models and PDR observations

We now investigate the effects of this new computation of the ortho-para conversion rate on grains in full PDR models. The code developed here to perform the statistical calculation of the conversion rate has been coupled to the Meudon PDR Code (Le Petit et al. 2006; Goicoechea & Le Bourlot 2007; Gonzalez Garcia et al. 2008; Le Bourlot et al. 2012).

The Meudon PDR Code² solves the stationary state of a one-dimensional PDR by computing self-consistently the chemical balance (147 species and 2835 reactions here), the thermal balance between heating (photoelectric effect, cosmic rays, exothermic reactions, as well as H₂ collisional deexcitation and dust-gas collisions that can act as heating or cooling terms) and cooling (by the lines of 28 species for which level populations are computed from statistical balance), and the radiative transfer in the

continuum (from radio to UV wavelength, taking into account dust absorption and scattering as well as continuum absorption by the ionization of species such as C and S) and in the lines of the species for which the level populations are computed.

At each position in the cloud, the local radiation field, gas density, gas-phase H₂ density and OPR computed by the Meudon PDR Code are used for the statistical computation of the ortho-para conversion rate, which is sent back to the Meudon PDR Code for a new iteration. The dust population comprises a mixture of carbonaceous and silicate grains following a power-law size distribution with exponent -3.5 (Mathis et al. 1977) from 1 nm to 0.3 μm .

In addition, the Meudon PDR code includes the other processes affecting the ortho-para ratio : formation on grains is assumed to occur with an OPR of 3, photodissociation and shielding are computed level by level and thus naturally include preferential shielding of ortho-H₂, and gas-phase ortho-para conversion includes reactive collisions with H (Le Bourlot et al. 1999, and references therein), H⁺ (Gerlich 1990) and H³⁺ (assuming identical rates as with H⁺).

In this section, we first present a detailed study of an example PDR model, discuss the local OPR in the regions emitting the rotational lines of H₂ and show the impact of the conversion process on grains on the local OPR and on the intensities of the rotational lines. We then compare for a full grid of models the OPR values that can be deduced from the predicted line intensities to actual PDR observations. Finally, we discuss the influence of the microphysical parameters τ_{conv} and T_{phys} on these results.

5.1. A typical PDR

We consider here as a typical PDR example an isobaric model with $P = 10^7 \text{ K} \cdot \text{cm}^{-3}$ illuminated by the standard ISRF scaled by a factor $\chi = 10^3$. In such a PDR, the first rotational lines of H₂ are mainly emitted in the warm molecular layer that follows the H/H₂ transitions, and will thus provide informations about the local OPR in this region.

Due to the large energy differences between the first rotational levels and the temperature gradient present in this layer, the successive lines are emitted in overlapping but relatively separated layers, as can be seen on Fig. 10. This figure shows the local emissivity profiles as a function of position, compared to the local OPR (lower panel), for a model that includes our treatment of surface conversion. We multiply the local emissivity ϵ by the distance from the edge so that the contribution of a given region to the total line intensity can be evaluated visually as the area under the curve in this region despite the logarithmic scale used for the distance axis. The emissivity profile of each line has also been scaled so that its maximum is 1. For reference, the density profiles of H and H₂ and the temperature profile are shown in the upper panel.

The local OPR shows a bump above 3 just before the H/H₂ transition, due to preferential self-shielding of ortho-H₂ compared to para-H₂ as H₂ is assumed to form with an OPR of 3 (as discussed in Abgrall et al. 1992; Sternberg & Neufeld 1999). The OPR is then at 3 immediately after the H/H₂ transition before decreasing sharply between 8×10^{-3} and 10^{-2} pc. The position of this sharp decrease is controlled by the efficiency of the ortho-para conversion process on grains, as we show later.

We see that the emission regions of the H₂ lines, starting at the H/H₂ transition for the higher lines, extend further than the OPR drop for the lower lines. The first five rotational lines usually observed in PDR are thus emitted in a region with a strongly varying OPR. We can thus expect that the OPR values deduced

² The Meudon PDR Code can be downloaded by following the instructions given at <http://ism.obspm.fr>

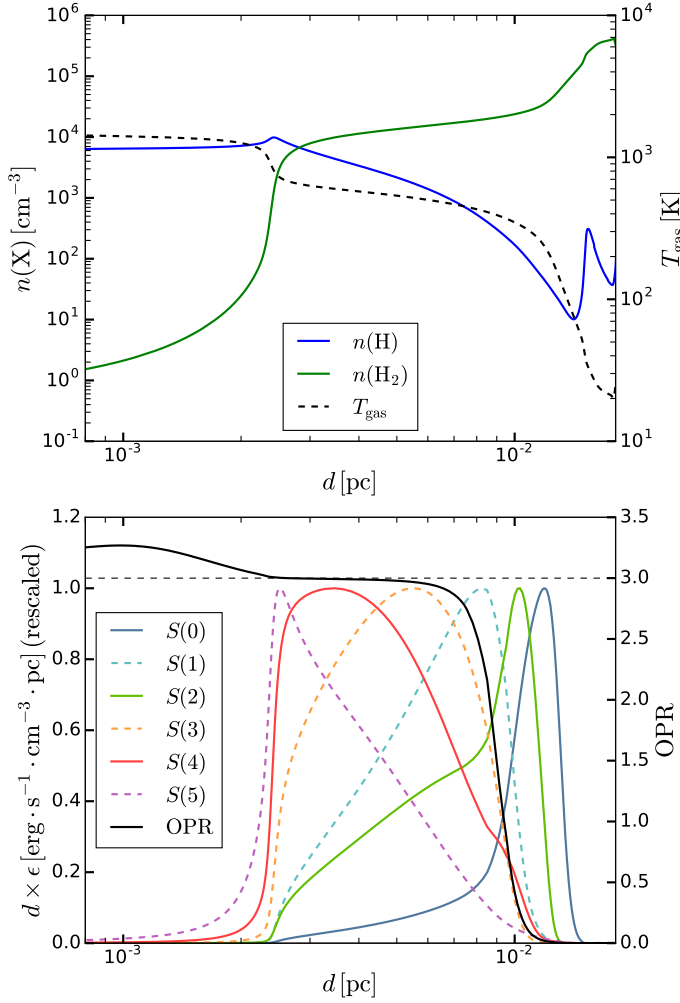


Figure 10. Upper panel: density profiles of H (blue) and H₂ (green) and gas temperature profile (red) in the PDR ($P = 10^7 \text{ K} \cdot \text{cm}^{-3}$, $\chi = 10^3$). Lower panel: local emissivity profiles (color lines) of the first rotational lines of H₂ (solid lines for para transitions and dashed lines for ortho transitions) compared to the local OPR profile (black). Local emissivities are multiplied by d so that the contribution of a given region to the total intensity is proportional to its area under the curve despite the logarithmic axis. Each emissivity curve has been scaled so that its maximum is 1 for ease of comparison.

from the line intensities will vary from 3 for the highest lines to a significantly lower value for the lowest lines. As described in the next section, we will thus compute observational OPR values based on each successive triplet of lines in our comparison between models and observations.

We can also note that the sharp decrease of the OPR causes an increase of the para lines relative to the ortho lines, resulting in an inversion of the emission peaks of the S(1) and S(2) lines, the S(1) emission peak occurring before (and thus in warmer gas than) the S(2) peak which occurs after the OPR drop. This inversion is highly dependent on the efficiency of ortho-para conversion on grains. Resolving this inversion at the distance of a PDR such as NGC 7023 would for instance require a $\sim 1''$ spatial resolution for the rotational lines of H₂, and will become possible with the James Webb Space Telescope.

Figure 11 shows the influence of the surface conversion efficiency on the position of the OPR drop. We compare the OPR

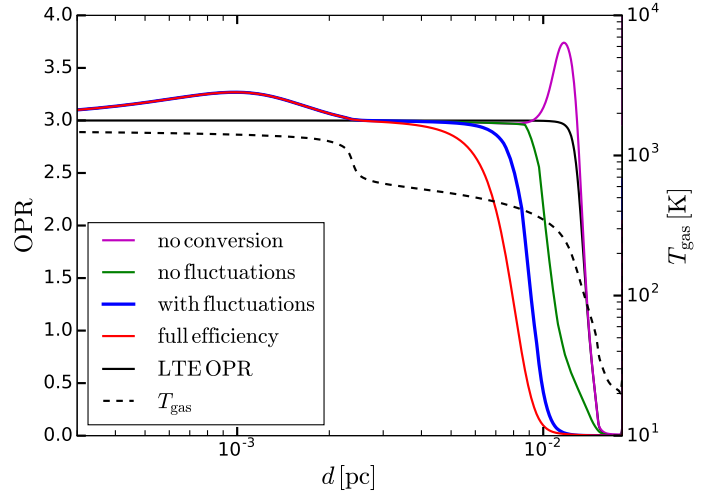


Figure 11. Comparison of the local OPR profiles in the PDR in models with $P = 10^7 \text{ K} \cdot \text{cm}^{-3}$ and $\chi = 10^3$ for the four prescriptions for ortho-para conversion on grains : no conversion (purple), rate equation approach neglecting the fluctuations (green), statistical approach taking the fluctuations into account (blue), and full conversion for H₂ molecules sticking to grains (red). The temperature profile of the PDR is also shown for reference (dotted black line), along with the corresponding LTE OPR profile (solid black line).

profile corresponding to LTE with the local temperature (black) to the OPR profiles obtained in PDR models implementing four different prescriptions for ortho-para conversion on grains : no surface conversion (purple), the rate equation treatment presented in Sec. 2.5 which neglects dust temperature fluctuations (green), the full statistical treatment described in Sec. 3 which takes fluctuations into account (blue), and a model assuming that all H₂ molecules sticking to grains are converted (red). As expected, the more efficient surface conversion is, the closer to the H/H₂ transition the OPR drop occurs. We also see that the results of the statistical computation are distinctly different from those of the simpler approximations and cannot be approximated by a simpler formalism. In the absence of surface conversion, the OPR drop starts when the temperature falls below 200 K as expected for a LTE OPR. Just before the drop in the case without surface conversion, the OPR peaks at ~ 3.7 due to photodissociation-formation cycling becoming the dominant mechanism again, as reactive collisions with H collapse proportionally to the H density after the H/H₂ transition. This only affects the local OPR in the absence of efficient surface conversion, and no such effect is present in our model including the statistical treatment of surface conversion.

These OPR profiles can be better understood by considering the rates of the different conversion processes that control the local OPR. Figure 12 shows the conversion rates per H₂ molecules by gas-phase reactive collisions (magenta), by destruction-formation cycling (green) and by dust surface conversion (blue), for a model that includes our statistical treatment of surface conversion. Both ortho-para (solid lines) and para-ortho (dashed lines) rates are shown. In this representation (assuming chemical balance), the local OPR is equal to the ratio of total para-ortho conversion rate to total ortho-para conversion. Before the H/H₂ transition, conversion is mainly due to reactive collisions (with H), but photodissociation is non-negligible and causes the OPR bump (OPR > 3) due to preferential shielding of ortho-H₂. After the transition, reactive collisions dominate un-

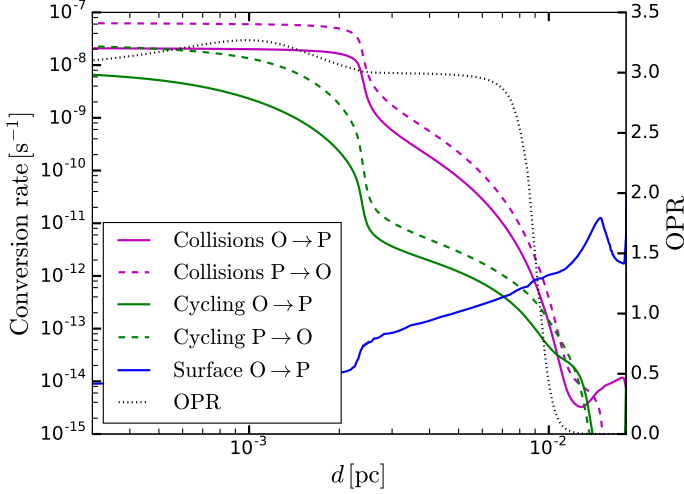


Figure 12. Conversion rates by the different processes : gas-phase reactive collisions (magenta), destruction-formation cycling (green), and dust surface conversion (blue).

til conversion on grain surface becomes comparable, at which points the local OPR decreases sharply to low values. This transition of the local OPR from 3 to very low values is thus due to surface conversion becoming dominant over reactive collisions. This explains why the position of this transition appeared to be controlled by the efficiency of surface conversion on Fig. 11.

Previous studies of the OPR in PDR observations (e.g. Fleming et al. 2010) have advocated advection flows bringing cold (low-OPR) gas from the molecular cloud through the PDR front to explain the low OPR values that are observed. We will see in the next section that the observed values can be explained by our model without advection flows. We can however estimate here the minimum velocity required for an advection flow to affect H₂ rotational lines intensities. Such a flow would need to bring cold (low-OPR) gas into the region where we predict an OPR of three. The OPR transition occurs on a width of $\sim 3 \times 10^{-3}$ pc, and the para-ortho conversion rate at the start of this transition is of the order of 10^{-11} s^{-1} . A minimum advection velocity of $\sim 1 \text{ km} \cdot \text{s}^{-1}$ would thus be required to affect the observable OPR in rotational intensities. This value corresponds to the maximum advection velocity through the dissociation front computed by Störzer & Hollenbach (1998) for PDRs with an advancing photo-ionization front. We thus estimate that advection could only affect the observable OPR of the rotational lines in the most dynamical PDRs with fast photo-ionization fronts.

Finally, we show the impact of these differences on the line intensities of the rotational lines of H₂ on Fig. 13. The lines S(3), S(4) and S(5), which are mainly emitted before the OPR drop in all cases are almost unaffected. The lines S(0), S(1) and S(2) are strongly affected with a S(1)/S(2) ratio varying by a factor of 4, and a S(3)/S(2) ratio varying by a factor of almost 3. The impact tends to be stronger for lower pressure models, as will be seen in the next section.

5.2. Comparison of a grid of models to PDR observations

As discussed in the previous section, the different rotational lines are emitted in regions with large differences in local OPR values. Interpreting observed rotational diagrams with a single OPR value is thus insufficient. We try here to measure the OPR as locally as possible by computing separate OPR values for each triplet of successive lines. We note $\text{OPR}_{j-1,j,j+1}$ the OPR com-

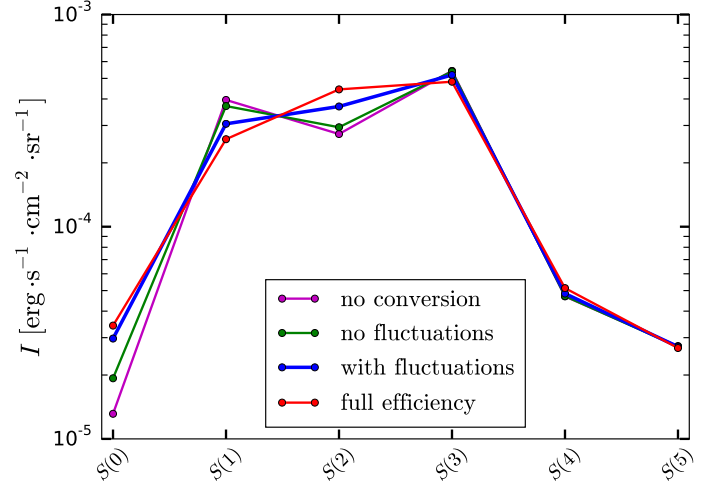


Figure 13. Intensities of the first rotational lines of H₂ predicted by the same PDR model ($P = 10^7 \text{ K} \cdot \text{cm}^{-3}$ and $\chi = 10^3$) for the four prescriptions for ortho-para conversion on grains: no conversion (purple), rate equation approach neglecting the fluctuations (green), statistical approach taking the fluctuations into account (blue), and full conversion for H₂ molecules sticking to grains (red).

puted from the column densities of levels $J = j - 1$, j and $j + 1$ (derived from the line intensities of lines $S(j - 3)$, $S(j - 2)$ and $S(j - 1)$). This OPR value is computed from the misalignment of level j with respect to the line defined by levels $j - 1$ and $j + 1$ in the rotational diagram as

$$\text{OPR}_{j-1,j,j+1} = \begin{cases} \text{OPR}_{\text{LTE}}(T_{j-1,j+1}) \frac{N_j/g_j}{N_{j-1}/g_{j-1}} \exp\left(\frac{E_j - E_{j-1}}{k_B T_{j-1,j+1}}\right) & \text{if } j \text{ odd} \\ \text{OPR}_{\text{LTE}}(T_{j-1,j+1}) \frac{N_{j-1}/g_{j-1}}{N_j/g_j} \exp\left(-\frac{E_j - E_{j-1}}{k_B T_{j-1,j+1}}\right) & \text{if } j \text{ even} \end{cases} \quad (48)$$

where N_j is the column density of level j (deduced from the intensity of line $S(j - 2)$), g_j and E_j the degeneracies and energies of level j and $T_{j-1,j+1}$ is the excitation temperature computed from levels $j - 1$ and $j + 1$ (thus unaffected by OPR effects):

$$T_{j-1,j+1} = -\frac{1}{k_B} \frac{E_{j+1} - E_{j-1}}{\log\left(\frac{N_{j+1}/g_{j+1}}{N_{j-1}/g_{j-1}}\right)} \quad (49)$$

and $\text{OPR}_{\text{LTE}}(T)$ is the thermal equilibrium value of the OPR at temperature T .

Note that this measure of the OPR can be affected by the presence of a curvature in the excitation diagram, corresponding for instance to a strong temperature gradient in the region of emission. A positive curvature will lead to an overestimation of $\text{OPR}_{j-1,j,j+1}$ for even values of j and an underestimation for odd values of j , as it will create a misalignment caused not by an actual out-of-equilibrium OPR value but by a varying excitation temperature for increasing values of J . We will thus compare the OPR values derived from the observations to OPR values similarly derived from the line intensities predicted by the models rather than to the actual local OPR value. We will see that lower-than-three OPR values are found for both odd and even values of j in the observations, indicating a physical OPR lower than 3.

We will focus on the lines that are the most affected by surface conversion on grains, the lines S(0) to S(3), which are also observed in a larger sample of PDR observations. The observation sample gathered from the literature is presented in Table 3,

Table 3. Sample of PDR observations of lines $S(0)$ to $S(3)$ with the derived values of T_{24} , OPR_{234} , T_{35} and OPR_{345} .

Object	Ref.	Note	T_{24} (K)	OPR_{234}	T_{35} (K)	OPR_{345}
L1721	(1)	upper limit for $S(3)$	206 ± 13	0.99 ± 0.22	< 308	< 3.00
California	(1)	-	208 ± 19	0.82 ± 0.15	303 ± 31	2.32 ± 1.18
NGC 7023 East	(1)	-	269 ± 9	0.86 ± 0.07	328 ± 37	1.35 ± 0.21
Horsehead	(1)	-	263 ± 20	0.65 ± 0.21	399 ± 33	1.54 ± 0.50
ρ Oph.	(1)	-	251 ± 16	0.75 ± 0.23	291 ± 14	1.08 ± 0.32
NGC 2023 North	(1)	-	222 ± 18	0.68 ± 0.21	302 ± 33	1.54 ± 0.65
NGC 7023 South-West	(2)	upper limit for $S(0)$	> 242	-	452 ± 14	1.43 ± 0.25
NGC 7023 North-West	(3)	-	293 ± 24	0.94 ± 0.28	438 ± 6	2.01 ± 0.28
ρ Oph. “pos. 1”	(4)	-	282 ± 23	1.05 ± 0.11	322 ± 8	1.41 ± 0.47
ρ Oph. “pos. 2”	(4)	-	300 ± 21	0.74 ± 0.22	313 ± 14	0.82 ± 0.20
ρ Oph. “pos. 3”	(4)	-	255 ± 7	0.58 ± 0.06	285 ± 7	0.77 ± 0.08
S140	(5)	missing $S(0)$	-	-	354 ± 59	1.57 ± 1.11
Orion Bar	(6)	-	258 ± 19	1.35 ± 0.53	361 ± 17	2.85 ± 0.57

(1) : Habart et al. (2011), (2) : Fuente et al. (2000), (3) : Fuente et al. (1999), (4) : Habart et al. (2003), (5) : Timmermann et al. (1996), (6) : Joblin et al. (in prep.)

with the values of T_{24} , OPR_{234} , T_{35} and OPR_{345} derived from the observed line intensities.

As shown by Joblin et al. (in prep.), the pressure in the dense structures of PDRs seems to be related to the intensity of the UV radiation field, with a roughly constant P/G_0 ratio. The typical value for the ratio P/G_0 in PDRs appears to be $\sim 2 \times 10^4$ with a scatter of a factor of 2-3 above and below. In our PDR models, we recall that G_0 is related to the scaling factor χ by the relation $G_0 \sim 0.65\chi$. The observed $P - G_0$ relation thus corresponds to $P/\chi \sim 10^4$. We thus use a grid of models covering a range of P/χ from 2×10^3 to 5×10^4 (a factor 5 above and below the observed value), and a range of pressures from $P = 10^5$ to $10^9 \text{ K} \cdot \text{cm}^{-3}$.

In the region where lines $S(0)$ to $S(3)$ are emitted, the local OPR is controlled by the balance between gas phase reactive collisions, which tends to thermalize the OPR to 3 and whose efficiency is dependent on the gas temperature, and surface conversion, which tends to thermalize the OPR to a lower value corresponding to dust temperature. The resulting observable OPR is thus dependent both on the surface conversion efficiency (which we wish to constrain) and on the gas temperature (which is controlled by the photoelectric efficiency in this region). Rather than simply comparing the measured OPR values, we thus investigate the $\text{OPR}-T_{\text{gas}}$ relation in both observations and model. When considering $\text{OPR}_{j-1,j,j+1}$, we thus estimate the gas temperature of the corresponding layer of the PDR through the excitation temperature $T_{j-1,j+1}$.

We thus present our comparison between models and observations on two figures presenting the $\text{OPR}_{234}-T_{24}$ relationship (Fig. 14) and the $\text{OPR}_{345}-T_{35}$ relationship (Fig. 15). On both figures, we compare the observed values (symbols with error-bars) to model results. As previously, we compare models with four different prescriptions for ortho-para conversion on grains : no surface conversion (purple), the rate equation treatment presented in Sec. 2.5 which neglects dust temperature fluctuations (green), the full statistical treatment described in Sec. 3 which takes fluctuations into account (blue), and a model assuming that all H₂ molecules sticking to grains are converted (red). The solid lines show results of models with $P/\chi = 10^4$, while the dotted lines correspond to model with P/χ ratios a factor of 5 above and below this value. Finally, the LTE value of the OPR as a function of the local temperature is shown as a black line.

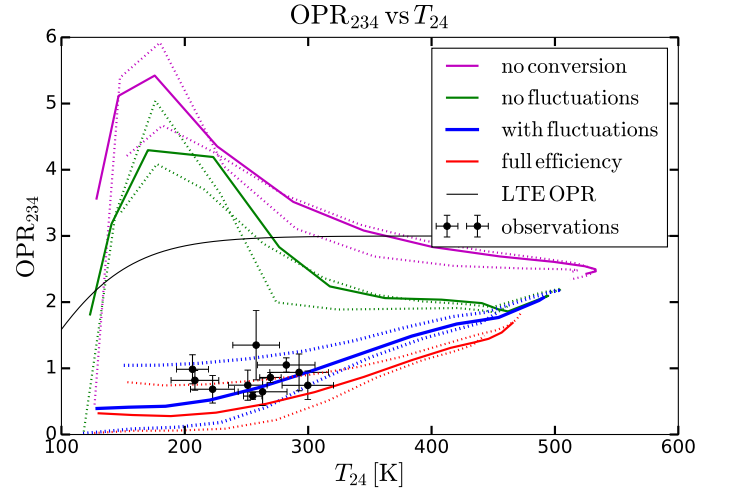


Figure 14. OPR computed from levels $J = 2, 3$ and 4 as a function of the excitation temperature T_{24} , comparing PDR observations (symbols) to for PDR models (lines). PDR models implement four prescriptions for ortho-para conversion on grains: no conversion (purple), rate equation approach without fluctuations (green), statistical approach with fluctuations (blue), and full conversion (red). Solid lines correspond to models with $P/\chi = 10^4$, while models with P/χ a factor of 5 above and below this value are shown as dotted lines.

On Fig. 14, corresponding to lines $S(0)$, $S(1)$ and $S(2)$, we see a clear separation between high efficiency models (statistical approach and full efficiency hypothesis) and the models without conversion on dust. The observational data points all fall close to the curve of these high efficiency models and are clearly incompatible with the no-conversion models. The observations thus indicate that high-efficiency conversion on grains is indeed occurring in PDRs. We also see that the models with the rate equation treatment of surface conversion, which neglects dust temperature fluctuations, give results that are close to models with no conversion. The statistical effect of fluctuations is thus necessary to explain the high conversion efficiency that the observations seem to indicate. Finally, the observations seem to favor the full statistical treatment over a simpler full efficiency hypothesis, but the difference is smaller and other uncertainties (for instance on the total dust surface available) could induce similar differ-

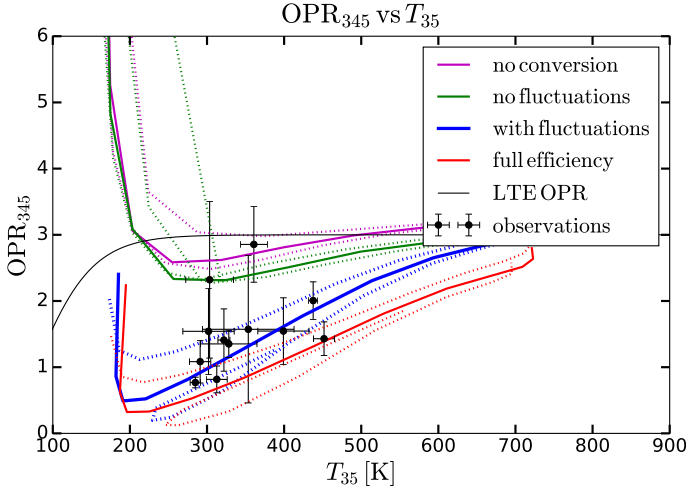


Figure 15. Same as Fig. 14 for the OPR computed from levels $J = 3, 4$ and 5, shown as a function of the excitation temperature T_{35} .

ences. However, the statistical treatment of fluctuations is again the only way to physically explain a high conversion efficiency.

On Fig. 15, corresponding to lines $S(1)$, $S(2)$ and $S(3)$, the observations are more scattered, but most datapoint again fall close to the results of models with the statistical treatment of fluctuations. The two outliers are the California PDR, whose large error-bars still make it compatible with the models, and the Orion Bar PDR which seems to have a clearly different behavior from all other PDRs. Again, the observations indicate a high conversion efficiency on grains which cannot be explained when neglecting the fluctuations, and slightly favor our statistical model over a full efficiency hypothesis.

On both figures, higher excitation temperatures correspond to higher pressure models. We see that the low-conversion-efficiency models (no conversion and rate equations neglecting the fluctuations) sometimes exhibit OPR values higher than 3. For OPR_{345} , this is due to the strong curvature of the rotational diagram for low pressure models. For OPR_{234} , curvature effects play in the opposite direction, and only explain the drop of the OPR at the lowest temperature. The values above 3 are actually caused by the local peak of the OPR, seen in Fig. 11 after the H/H₂ transition for models without efficient surface conversion, and which is due to preferential photodissociation of para-H₂ in a fully molecular region where reactive collisions with H are very rare. Moderate curvature effects are also seen in the fact that the OPR values of models at high temperatures seem to converge towards a value lower than 3 for OPR_{234} and higher than 3 for OPR_{345} . These measures of the OPR are thus slightly biased due to the curvature of the rotational diagrams. Observations and models are however similarly biased, and these figures present equivalent information as $S(1)/S(0)$ vs $S(2)/S(0)$ and $S(2)/S(1)$ vs $S(3)/S(1)$ graphs, in a more physically meaningful form.

Finally, we can note that the range of excitation temperatures found by the models is significantly more extended than the range of observed excitation temperatures, despite the fact that the observed objects cover a wide range of conditions. This probably indicates that the temperature profile (and possibly the density profile) in the region that emits H₂ rotational lines is not adequate in the models. It could come from an incorrect estimation of photoelectric heating or from the dynamics of the photodissociation front affecting the density profile of the PDR. The observations seem to indicate that PDRs with very different

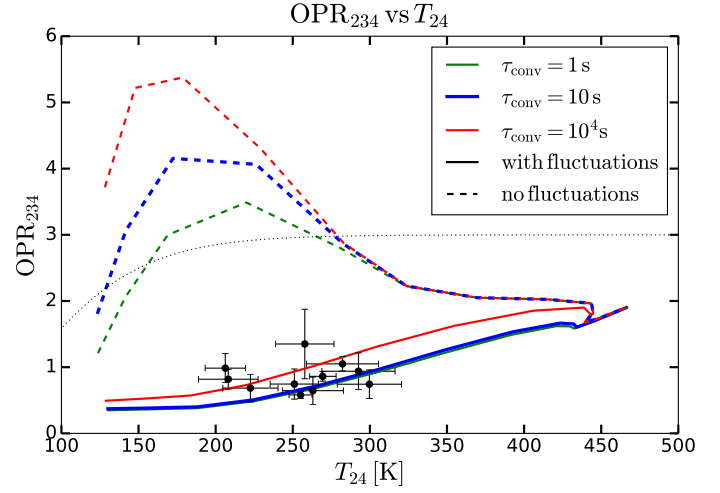


Figure 16. Influence of the surface conversion timescale τ_{conv} on the observable OPR_{234} as a function of T_{24} . We compare models results for three values of τ_{conv} (1 s in red, 10 s in blue and 10^4 s in green) and for two different prescriptions of the ortho-para conversion on grains (rate equation neglecting fluctuations in dashed lines, full statistical treatment of fluctuations in solid lines) to the PDR observations.

excitation conditions still have relatively similar temperatures (200 – 300 K) in the region where the first rotational lines of H₂ ($S(0)$ to $S(2)$) are emitted.

5.3. Influence of the microphysical parameters

Our microphysical model of ortho-para conversion on dust grains depends on two poorly constrained parameters : the surface conversion timescale τ_{conv} and the physisorption binding energy T_{phys} (cf. Sec. 2.2 and 2.3). We now investigate the impact of these uncertainties on the previously presented results.

We first study the impact of the conversion timescale τ_{conv} . We took $\tau_{\text{conv}} = 10$ s as our standard value, while the possible values found in the literature range from 1 s to 10^4 s. Fig. 16 and 17 thus compare the results of PDR models using these three values of τ_{conv} . Only the models with the statistical treatment of fluctuations (solid lines) and with the rate equation treatment without fluctuations (dashed lines) are shown, in comparison to the observations. On both figures, the impact of the variations of τ_{conv} on the models with the statistical treatment is limited and the model results remain compatible with the observations. Models implementing the rate equation treatment are more strongly affected (for OPR_{234}) but remain incompatible with the observations.

For the physisorption binding energy T_{phys} , we took a standard value of 550 K. The values found in the literature range from 300 K to 800 K. Fig. 18 and 19 show the model results for these three values. Again only the rate equation treatment (dashed lines) and the statistical treatment (solid lines) are shown. The binding energy T_{phys} has a dramatic impact on the results when neglecting fluctuations, while its impact when taking the fluctuations into account is small. At $T_{\text{phys}} = 800$ K, the rate equation results start to approach the observations as desorption becomes slower and efficient conversion can happen, but the results remain less fitting than the results of the statistical treatment.

The conclusions of the previous section are thus unaffected by the uncertainties on the microphysical parameters. The dust

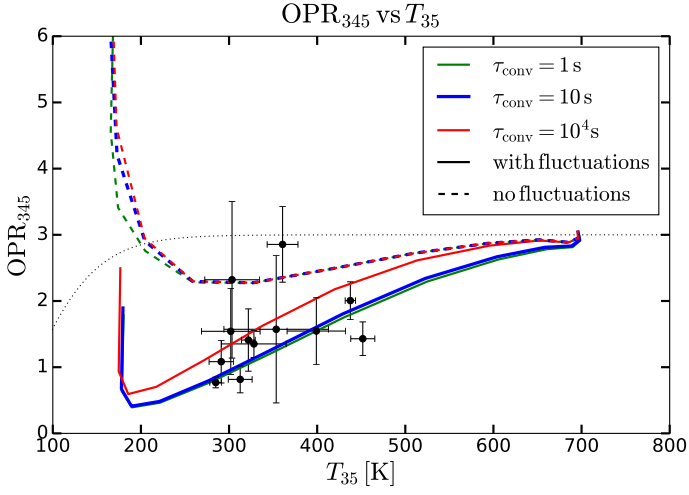


Figure 17. Same as Fig. 16 for OPR₃₄₅ as a function of T_{35} .

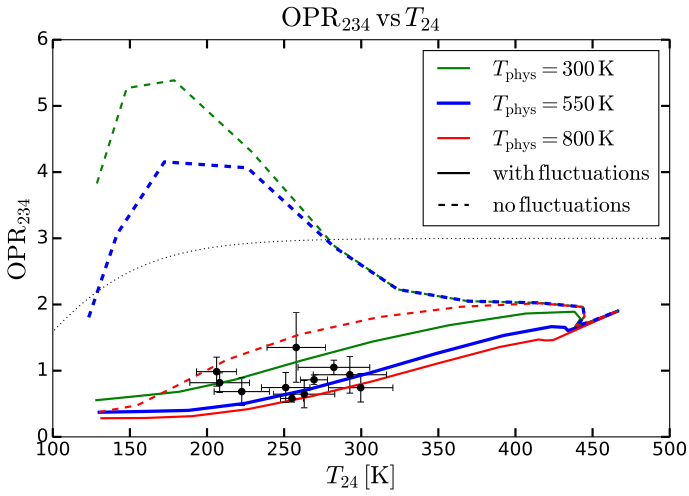


Figure 18. Influence of the physisorption binding energy T_{phys} on the observable OPR₂₃₄ as a function of T_{24} . We compare models results for three values of T_{phys} (300 K in red, 550 K in blue and 800 K in green) and for two different prescriptions of the ortho-para conversion on grains (rate equation neglecting fluctuations in dashed lines, full statistical treatment of fluctuations in solid lines) to the PDR observations.

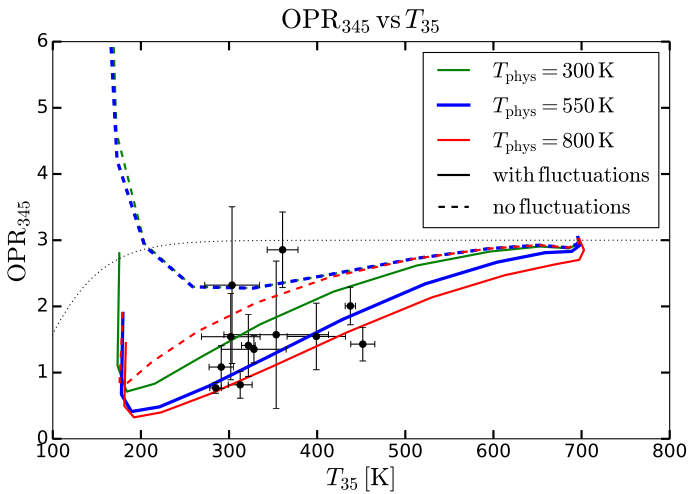


Figure 19. Same as Fig. 18 for OPR₃₄₅ as a function of T_{35} .

temperature fluctuations make the conversion rate much less dependent on the detail of the microphysics. Dust temperature indeed explore a large range of temperatures during the fluctuations, and the average efficiency is thus controlled by the fraction of the grains whose temperature fall in the range where the instantaneous rate is high (in other terms, the portion of the temperature PDF that falls in this range). Varying the microphysical parameters, and thus the extend of the temperature range where the instantaneous rate is high, only changes this fraction slowly while it can change dramatically the instantaneous rate at a given temperature (for instance the equilibrium temperature used when neglecting fluctuations). A similar effect of the dust temperature fluctuations was found in Bron et al. (2014) for H₂ formation.

There is however one source of uncertainties that is not reduced by the effects of temperature fluctuations: as discussed in Sect. 2.1 the sticking function on bare grains is not well known and the conversion efficiency is directly proportional to the sticking probability. In the region where surface conversion affects the local OPR and H₂ rotational emission lines, the gas temperature is in the range 100 – 400 K. The sticking function that we used (Matar et al. 2010) gives sticking probabilities in the range 0.1 – 0.4 for this temperature range. A sticking function significantly lower than these values would thus reduce the impact of surface conversion on H₂ emission. Finally, the total available dust surface and especially the dust surface corresponding to small grains would also affect the total surface conversion rate. The PDR observations to which we compared our results seem to be in agreement with the prescriptions used for the sticking function and the dust population.

6. Conclusions

We have built a model of ortho-para conversion of H₂ on dust grains based on the latest experimental and theoretical results. When neglecting dust temperature fluctuations, conversion is found to be strongly suppressed by the presence of a UV radiation field.

We developed a statistical calculation of the conversion rate, based on a master equation approach (similar to the method used in Bron et al. 2014 for H₂ formation), that takes into account the statistical effect of dust temperature fluctuations. Conversion on grains is found to stay efficient under much higher UV radiation fields when fluctuations are taken into account. Small grains, despite being too warm on average, spend a sufficiently large fraction of their time between temperature spikes at colder temperatures where conversion is efficient.

This conversion process on grains is found to play an important role in PDRs, affecting the rotational lines intensities. The local OPR falls from 3 to a low value inside the region where H₂ rotational lines are emitted, and the position of this transition is controlled by the conversion efficiency on dust grains. As a result, the OPR determined from the line intensities of the first few rotational lines is a signature of the efficiency of this process.

The comparison of our models to a sample of PDR observations of rotational H₂ lines indicates a high conversion efficiency on dust grains. Models implementing the exact statistical treatment with dust temperature fluctuations give results that are consistent with the observations. Models that neglect the fluctuations cannot account for the high conversion efficiency indicated by the observations. Ortho-para conversion on dust grains is thus an efficient and important process in PDRs, which can only be accurately described by a statistical treatment of the impact of dust temperature fluctuations. This process is responsible for the

OPR values lower than 3 derived from rotational lines observations of PDRs.

We also found that this efficiency induced by temperature fluctuations is much less sensitive to the microphysical parameters of the model (binding energy, surface conversion timescale) than the efficiency at a single fixed temperature (e.g. the equilibrium temperature). As a consequence, the results obtained here are robust despite large uncertainties on the microphysical parameters (binding energy in the range 300 – 800 K, conversion timescale in the range 1 – 10⁴ s). A similar effect was found in Bron et al. (2014) for H₂ formation on grains, and it seems to be a general consequence of having a distribution of dust temperatures rather than a single dust temperature.

In this study, the statistical formalism used to take temperature fluctuations into account, developed in the case of a single chemical variable for H₂ formation in Bron et al. (2014), was extended to a case with two chemical variables, demonstrating that this method could be generalized to larger chemical networks. For instance, it could be used to study the impact of cosmic-rays-induced fluctuations on ice chemistry.

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